MOISTURE REMOVAL FROM AND LIQUEFACTION OF BEULAH ZAP LIGNITE.

K. S. Vorres[*], D. Wertz[**],
J. T. Joseph[***], and R. Fischer[***]

[*]Chemistry Div., Bldg. 211, Argonne National Lab., Argonne, IL 60439,
[**]Dept. of Chemistry, Univ. So. Miss., Hattiesburg, MS, 39406,
[***]Amoco Oil Co. R&D, Naperville, IL,60566

INTRODUCTION

Lignite reserves represent an important resource for the production of synthetic liquid fuels. The high reactivity of lignite would indicate a high throughput from a given process train. However the moisture content of this material has been a concern for efficient processing into liquid hydrocarbons. Furthermore, drying might introduce irreversible changes to the pore structure which would limit the rates of reaction.

This collaborative study has been undertaken to help understand the role of moisture in the liquefaction and also to understand the kinds of changes that take place in the coal particles during drying.

The physical structure of coal consists an organic matrix and inorganic matter containing an extensive network of pores. The pore network usually contains water. Mraw and Silbernagel (1) suggested that the amount of water present in as-mined coals provides a measure of pore volume. However, Kaji et al. (2) examined the water-holding capacity, specific surface area, and pore volume of 13 coals from various locations, ranging from lignite to anthracite, and found no correlation between the water-holding capacity and the pore volume. Assuming that the total coal oxygen is distributed uniformly through the coal and the functional-group oxygen increases with oxygen content, Kaji et al. found a linear relationship between the hydrophilic sites and the water-holding capacity of coal. The relationship between the total oxygen content of coal and the water-holding capacity may be fortuitous since oxygen-functional groups are not the only hydrophilic sites in coal (3). Moreover, the presence of minerals, especially smectite lattices, and various cations will also strongly influence the coal-water interactions.

Vorres et al. (4) and Vorres and Kolman (5) studied the kinetics of vacuum drying of coal to understand the complex coal-water interactions. From isothermal thermogravimetry analysis, i.e., the weight loss vs. time at fixed temperature, Vorres and his co-workers observed that the dehydration of Illinois No. 6 in the form of a block, -20 mesh, and -100 mesh, follows a desorption kinetics mechanism. Thus, they concluded that the rate controlling mechanism of dehydration is governed by the surface of coal. In addition, Vorres and his co-workers indicated that the particle size and the history of coal also affect the dehydration kinetics of coal. More recently, Abhari and Isaacs (6) used the thermogravimetric analysis (TGA) technique to explore the drying

kinetics of six coals from the Argonne coal-sample series. They used a bulk moisture/pore moisture model to explain the observed drying kinetics for the six coals, in which the order of kinetics, i.e., the order of dehydration showed a strong dependence on the rank of coal. These researchers assumed that water in coal is held by the physisorption process. This assumption is at variance with the temperature dependent NMR results (7) and the contention of Kaji et al. (2). Even more recently, Vorres et al reported the kinetics of drying of lignite in dry nitrogen. They observed a unimolecular mechanism, with a transition after the loss of about 85% of the water present in the original sample (8). The transition resulted in a lower rate with the unimolecular mechanism. Studies with the thermobalance and differential scanning calorimeter indicated the same mechanism and transition (8).

In this paper, we report our recent results on: the kinetics of water's desorption from Beulah-Zap lignite coal, as determined by thermogravimetric analysis (TGA); physical structure changes as' observed with x-ray diffraction; and the effects on liquefaction due to drying.

EXPERIMENTAL

Isothermal Thermogravimetry

Coal drying was done with a Cahn model 121 thermobalance attached to an IBM PC/XT microcomputer. Vendor-supplied software was used to monitor the progress of individual runs, and convert data files to a form that could be further studied with Lotus 123.

The data were obtained as files of time, temperature and weight at 10 second intervals. Run times varied from 7-16 hours. Sample sizes varied from about 20-160 mg. Temperatures were varied between 20 and 80 C. The gas velocity past the sample was varied from 20 to 160 cc/min in the 25 mm diameter tube. The sample was placed in either a quartz or a platinum hemispherically-shaped pan. Sample included the two mesh sizes (-100 and -20) of the Argonne Premium Coal Samples and also one or two small pieces which came from lumps which were stored under nitrogen.

Samples were quickly transferred from ampoules which had been kept in constant humidity chambers with water at room temperature ($293^{O}K$). In the thermobalance system a period of about 5 minutes was used to stabilize the system and initiate data acquisition. A condenser was made to replace the usual quartz envelope that surrounds the sample. An antifreeze solution was circulated from a constant temperature bath through the condenser to maintain constant temperature during the experiments. This was more stable than the furnace and provided very uniform temperature control during the experiments.

The gas atmosphere was cylinder nitrogen (99.99%) or "house" nitrogen from the evaporation of liquid nitrogen storage containers used without further purification and passed over the sample at rates of about 20-160 cc/min.

Data were initially analyzed by testing the weight loss as a function of time with 13 different kinetic expressions including geometrical, unimolecular, first and second order diffusion to establish a best fit (8). Regression analysis was used to obtain the kinetic constants. Lotus 123 was used for analysis of individual run data.

Round Robin Sample Preparation

In order to compare the results of drying with the help of several techniques a set of samples was prepared and distributed. A batch of twenty five grams of -100 mesh lignite was dried in a vacuum oven at room temperature. One batch was dried for 4 hours, and the other for 24 hours. The samples were brought to atmospheric pressure under nitrogen, quickly transferred to a nitrogen filled glove bag, and transferred to previously dried screw cap vials. The vials were further sealed with tape around the cap. These samples were distributed to the University of Southern Mississippi for x-ray diffraction studies and Amoco Oil Company for liquefaction studies and comparison with fresh lignite sample.

RESULTS AND DISCUSSION

Isothermal Thermogravimetry

The data were normalized to one gram of starting sample weight. The best fit of the data were obtained with a unimolecular decay kinetic expression. Plots of ln (water left) versus time gave a characteristic shape. The plot indicates a consistent slope for the initial 85% of the moisture loss of the coal. A transition then occurs. The rate is then reduced to about 0.5-0.1 of the earlier rate. Figure 1 shows a typical plot of ln water left (mg/gm sample) as a function of time (10 second intervals).

The rates are similar for different particle sizes if the sample weight and gas velocity are held constant. Table 1 indicates the similarity in rates for 150 mg samples in the hemispherical quartz container. Activation energies are also given for each particle size.

Table 1. Rate Constants for First Segment
        (mg water/gm sample/10 sec)

Temperature--> Size	20 C	40 C	80 C	E_a Kcal/mole
-100	.00009	.00024	.00099	8.2
-20	.00007	.00024	.00131	10.0
Block	.00010	.00023	.00085	7.3

The activation energy calculated from these data averages 8.5 Kcal/mole.

The rate is a function of the size of the sample and the gas velocity around the sample. The size of the sample affects the depth of the material through which the moisture must diffuse to escape. The normalized rates were inversely proportional to the sample size. The rate is directly proportional to the gas

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velocity since the more rapidly moving stream is more effective in removing the water molecules or limiting the opportunity for rehydration.

The effect of temperature is measured through the activation energy from an Arrhenius plot. Figure 2 shows the data plotted for several sets of data representing three different constant gas velocities. The lines are almost parallel and indicate an average activation energy of 8.0 Kcal/mole. The higher gas velocities are able to more effectively remove water molecules and increase the rate of drying.

Varying the sample weight also varies the depth of the sample in the container. Figure 3 indicates the change in rates as the sample weight is changed at different temperatures. The rate in terms of mass of water lost per gram of sample in a given time is greater for the smaller, and therefore thinner samples. The probability of a water molecule recombining with the lignite rather than leave the sample diminishes as the diffusion path is shortened.

The use of vacuum to remove moisture was seen to be capable of much more rapid removal of water than a stream of dry nitrogen. The ratio of the rate coefficients is an order of magnitude greater, and would imply a rate advantage to this technique for engineering for rapid processing of pulverized fuel.

The initial removal of about 85% of the moisture and then a transition to a slower rate of water loss implies a structural rearrangement. It is believed that the pores of the particles are changed after this amount of water is lost in a manner that makes the further loss of water more difficult.

X-RAY DIFFRACTION STUDIES

The X-ray diffraction studies carried out at the University of Southern Mississippi shown in Figure 4 indicate that the physical structure of the coal (not the inorganic material) changes with the drying. Further the reduced "noise" level associated with the diffraction pattern on the recorder indicates that there is a greater regularity in the dried coal than the raw or partially dried material. Further studies of the diffraction data are underway to provide additional insight into the changes that have been observed. The figure indicates the diffractograms from: A. untreated lignite, B. partially dried lignite and C. dried lignite.

The peak at 22° is due to an internal standard that was added. The peak at 14° is due to the 002 plane of graphitic material associated with coal samples. Note that the peak shape for untreated lignite is reasonably symmetrical implying a distribution of spacings about an average value. The partially dried material has a distorted shape for the 002 peak indicating that the larger planar spacings are no longer present in the sample. In the dried sample the peak is again relatively symmetrical.

LIQUEFACTION STUDIES

The oil yield measurements have been carried at Amoco Oil Co. at
the Naperville Research Center. Small samples were added to
tetralin, and the material heated under hydrogen at 1000 psi to
400 C for four hours. The product gases were recovered and
analyzed by gas chromatography. The liquid and residual material
were extracted with a series of solvents to give oil, preasphal-
tene and asphaltene fraction amounts.

The studies indicated that the different coal samples did give
different oil yields, as well as preasphaltene and asphaltene
yields. The initial data indicate that the raw and partially
dried samples gave higher preasphaltene and asphaltene yields
than the dried material, with the highest yields for the partly
dried sample. Conversely the oil yield was highest for the dried
sample, lowest for the partly dried material and the starting
material had an intermediate value. The data are given in Table
2. The total of the oil, preasphaltene and asphaltene was almost
the same for all samples. The gas yield was the same for the two
moist materials and higher than the dried material, suggesting a
role for moisture in gas production. Hydrogen diminishes for
dried coal, while carbon monoxide increases. Methane and higher
hydrocarbons remain about the same for all levels of dryness, sug-
gesting that they are released by some mechanism which is not de-
pendent on moisture, i. e. they may simply be dissolved in the
matrix. Carbon dioxide yield increased for the partly dried
material and then decreased for the dry material suggesting two
competing reactions.

Table 2. Initial Liquefaction Results from Lignite Samples

Coal	Raw	High Moisture	Low Moisture
Moisture:	32.2%	23.9%	0.3%
Products, Wt%			
OIL	24	21	31
ASPHALTENE	24	25	20
PRE-ASPHALTENE	11	13	7
UNCONVERTED	31	31	33
TOTAL GASES	10.5	10.5	8.5
GAS BY TYPE:			
hydrogen	0.209	0.196	0.156
carbon monoxide	0.238	0.276	0.340
methane	0.486	0.474	0.480
carbon dioxide	5.373	5.543	4.849
ethane	0.163	0.166	0.154
propane	0.056	0.055	0.054
propylene	0.011	0.011	0.009

CONCLUSIONS

The lignite drying kinetics follow a unimolecular rate law which is first order in the water in the sample. There are two segments in the dehydration kinetics plots, and each follows a unimolecular rate law. The first drying segment includes about 80-85% of the water loss. The second drying segment includes most of the remaining water and occurs at about half the rate of the first segment. The mechanism is unchanged over the range 20-80°C. The activation energy for the initial moisture loss is about 8 Kcal/mole. The water jacketed heating system provides superior temperature control. The rate of drying is sensitive to the gas velocity over the sample. The rate of drying is dependent on the sample size and the sample depth. Rates are generally similar for -20 and -100 mesh samples. The same mechanism is observed for differential scanning calorimetry measurements. X-ray powder diffraction measurements show structural changes during the drying process. Drying improves the oil yield from lignite samples as a result of hydrogenation.

ACKNOWLEDGMENTS

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Figure 1, Lignite Dried in N2, 80 C
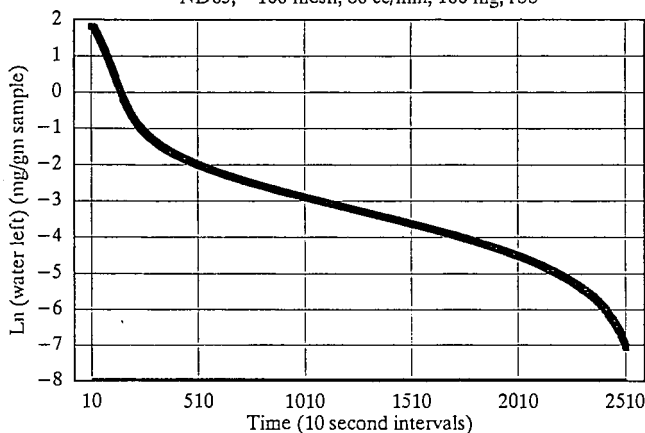
ND65, −100 mesh, 80 cc/min, 160 mg, rbb

Figure 2, Arrhenius Plot, Lignite Dried in N2
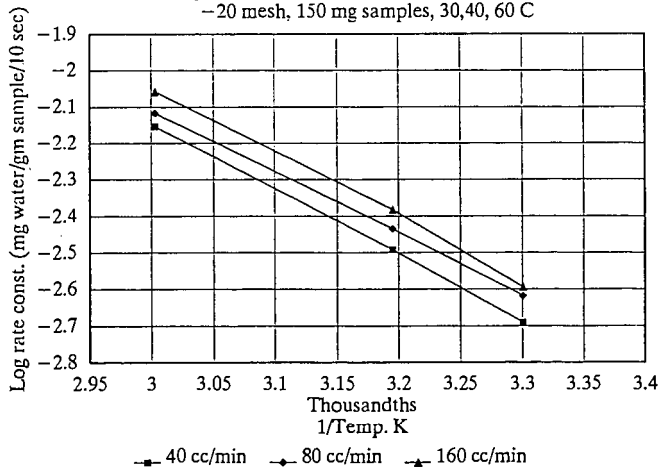−20 mesh, 150 mg samples, 30,40, 60 C

▪ 40 cc/min   ♦ 80 cc/min   ▲ 160 cc/min

Fig. 3, Rates Change as Sample Weight Changes
75, 150 mg samples, 30,40, 60 C

Rate constant (mg water/gm sample/10 sec) Thousandths — Y-axis

Sample Weight (mg) — X-axis

■ 30 C   ◆ 40 C   ▲ 60 C
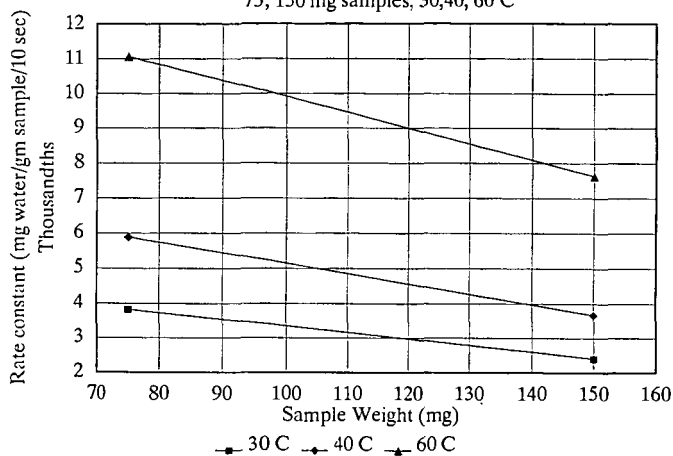
Figure 4, X–Ray Diffractograms of Lignite Samples

A.
B.
C.

CPS — Y-axis

DIFFRACTION ANGLE, Mo XRAYS
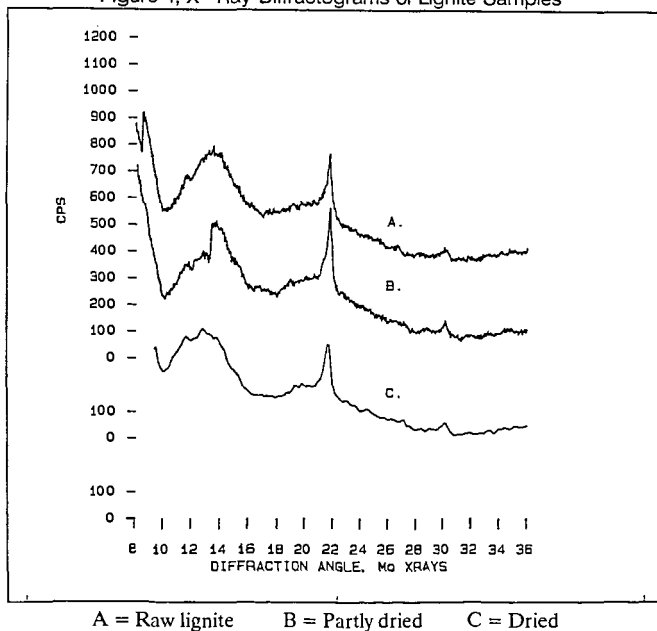
A = Raw lignite   B = Partly dried   C = Dried

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MONITORING THE OXIDATION OF COALS IN STORAGE

David C. Glick, Gareth D. Mitchell and Alan Davis
Energy and Fuels Research Center
Penn State University
205 Research Building E
University Park, PA 16802

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ABSTRACT

Two studies of conventional coal sample storage containers revealed problems with the atmospheric gas composition and preservation of the samples. Heat-sealable polyethylene/aluminum foil laminate bags were evaluated by various methods in two further studies. The first compared preservation of a freshly collected mvb coal in laminate bags to other container types. The second compared Argonne premium coal samples sealed in their original ampoules to those repackaged in laminate bags. Preservation in laminate bags is better than in conventional containers and comparable to glass ampoules. Samples collected after 1988 for the Penn State Coal Sample Bank have been stored exclusively in laminate bags after processing. Monitoring the condition of these samples is an ongoing project.

INTRODUCTION

When coals are stored in a sample bank for use over a period of months or years, it is important to preserve their original properties. If preservation is not achieved, measurements made after the passage of time will not be comparable to those obtained from the fresh sample. Among the properties which may change are pyritic and sulfate sulfur content, calorific value, thermoplastic properties as measured by free-swelling index and the Gieseler plastometer, fluorescence, FTIR spectra, liquefaction yields and products, alkali extraction and methane content. Some changes are purely chemical, many involving oxidation. Others may have a physical component related to relaxation after release of lithostatic pressure in mining and comminution in sample preparation.

STUDIES OF CONVENTIONAL CONTAINERS

The environment of a coal sample in storage differs greatly from its in situ environment prior to mining. Conventional laboratory and bulk materials containers such as barrels, buckets, cans, jars and bags are typically used for storage. The internal atmosphere is often replaced with nitrogen or argon to reduce oxidation.

In the Penn State Coal Sample Bank (1), field collection and bulk sample storage were previously accomplished with 113 L polyethylene barrels (100 kg capacity) and 19 L buckets (16 kg capacity), both fitted with gasketed lids and valves for argon introduction. Smaller splits of samples at -0.85 mm have been stored in heat-sealed argon-filled polyethylene bags sealed in standard #2 steel cans (600 mL, 400 g capacity).

The composition of the atmospheres within barrels and buckets over time was studied using gas chromatography. Different methods of argon introduction were used on three containers of each type:

for 113 L barrels:

1) The lid was sealed, and the container was pumped with a small vacuum pump for approximately 2 minutes, then argon was introduced until a slight positive pressure was reached.

2) Same, except with large vacuum pump.

3) The lid was placed loosely over the container to allow the introduction of a stainless steel wand, through which argon was introduced to the bottom of the container. The wand was gradually withdrawn while the argon flowed for approximately 4 minutes, and the lid was sealed.

for 19 L buckets:

1) The lid was sealed, and the container pumped with a small vacuum pump for approximately 30 seconds, until the bucket began to deform. Argon was introduced until a slight positive pressure was reached.

2) Same, except that the pumping and argon introduction were repeated after 3 hours.

3) A wand was used as in #3, under barrels, above.

The results of monitoring the atmospheric compositions (Fig. 1) showed that some argon introduction methods were more effective but all containers tended to leak so that after one month the argon had escaped.

In another study, splits of 53 coals of varying rank stored in barrels and cans were monitored. Gieseler fluidity, sulfate sulfur and calorific value changed during storage over a period ot four years. In the graph of Gieseler fluid range (Fig. 2), lower values after storage indicate oxidation or deterioration of the sample. In the graph of sulfate sulfur (Fig. 3), higher values after storage indicate oxidation of pyritic sulfur to sulfate. Both graphs show that splits stored in cans were better preserved than those in barrels, and that deterioration increases with time. A related study showed buckets to be similar to barrels in their preservation ability.

After initial processing, each of the 53 coals occupied two full barrels (at –25 mm particle size) and one half–full barrel (at –6 mm). Polarographic oxygen analysis was performed on one barrel of each particle size for each coal. Two trends were observed in the results (2). Gaseous oxygen levels in the drums were related to coal rank, with low oxygen values for most low–rank and high–volatile bituminous coals and high values (above 15%) for all medium– and low–volatile bituminous and anthracite coals. This is interpreted as better scavenging of oxygen by low–rank coals. The half–full drums also had higher oxygen levels than the full drums. The coals stored in barrels at –6 mm showed an average decrease in calorific value of only 130 BTU/lb (dry, ash–free basis) (2).

For the bituminous coal samples stored in cans, alkali extraction values (3) were plotted against decrease in Gieseler fluid temperature range (4). For bituminous coals, alkali extraction is a measure of the state of weathering at the time of collection, whereas Gieseler fluidity parameters are sensitive indicators of deterioration during storage. Decreases in fluid temperature range varied from zero to 60°C, with more than half decreasing less than 10°C, while alkali extract transmission of nearly all samples was above 94%. Thus many of the samples stored in cans were judged to be preserved rather well, while a few had deteriorated noticeably.

Although some changes in storage are probably inevitable, it was concluded that the degree of preservation achieved in polyethylene pails and barrels was unsatisfactory. The difference in preservation between cans and larger containers was also considered a problem. When the initial stock of cans of a given sample was depleted, a new batch of cans made from the contents of a bucket would be more deteriorated. Other container types which would better preserve coal samples of varying amounts were sought.

FOIL/POLYETHYLENE MULTILAMINATE BAGS

A study by Sharp (5) reported the use of laminated foil and plastic bags to preserve moisture and calorific value. These bags are constructed of three layers; polyethylene inside allows heat–sealing and shields the contents from the middle aluminum foil layer which provides a barrier to gas transport and light. An outer spun–bonded polyethylene layer resists tears and abrasion. Sealing may be accomplished by manual flushing with inert gas and a manually operated sealer, or an automated vacuum/inert gas sealer as used in the food industry.

EXPERIMENTAL METHODS

Comparison to conventional containers

A study was planned to measure changes in several properties through time for a coal sample stored in different container types. Because fluidity had changed significantly during storage in previous studies, a coal with fluidity was desired for this study. A run–of–mine sample of medium–volatile (mean–max R_o 1.27%) Lower Kittanning seam coal was collected in western Pennsylvania. The sample was immediately taken to Penn State, crushed, split and prepared for analysis. Gieseler fluidity, free–swelling index and alkali extraction results were obtained within 30 hours of the coal being mined. Epoxy–binder pellets for fluorescence microscopy and splits for other analyses were also prepared at this time.

Splits of the sample were packaged in several container types for the study: –6 mm coal in polyethylene buckets and foil laminate bags; –0.85 mm coal in steel cans, foil laminate bags and an open container exposed to the atmosphere. After 4, 16 and 52 weeks containers were opened and samples analyzed as had been done for the original sample.

Comparison to Argonne Premium Coal Sample glass ampoules

Argonne National Laboratory's Premium Coal Sample Program supplies coal samples in flame–sealed, nitrogen–filled glass ampoules (6). Six ampoules of each of the six available bituminous coals were obtained. Two of each were opened and analyzed to obtain initial Gieseler fluidity and alkali extraction values. Two of each were placed in a nitrogen–filled glovebox where they were opened and the contents resealed in foil

laminate bags. Two of each remained unopened. After eight months analyses comparing the coal resealed in foil laminate bags with that in the undisturbed ampoules were performed.

RESULTS

Thermoplastic Properties

Fluid properties (Gieseler plasticity and free–swelling index) are among the most sensitive indicators of deterioration during storage. The fresh Lower Kittanning sample had a maximum fluidity of 1224 ddpm with a fluid range of 100°C. Figure 4 shows that foil laminate bags maintain fluid range better than steel cans and much better than buckets. Maximum fluidity and free–swelling index showed similar trends.

For the Argonne premium samples, Table I shows that samples ANL–101 and –501 repackaged in foil laminate bags and stored for eight months compared well to those stored in their original ampoules. The variation in results for ANL–701 is probably caused by problems with the instrument, and for ANL–301, –401 and –601 the test could not be successfully completed on the amount of coal allocated because multiple repeat runs were required to meet the ASTM precision requirement (7).

Sulfur Forms

Another sensitive indicator of deterioration, particularly in coals with abundant iron sulfide minerals, is the oxidation of sulfides to sulfates. Figure 5 shows that foil laminate bags avoid production of sulfates better than cans and much better than buckets. As with fluid range, the bucket sample was even worse than the sample exposed to the atmosphere. The bucket sample had much higher moisture than the exposed sample, perhaps caused by leakage, trapping of moist air, and subsequent condensation. Surface moisture would accelerate the sulfide to sulfate reaction.

Gaseous Oxygen

Oxygen levels in the containers' internal atmospheres were measured with a polarographic oxygen detector (Fig. 6). Low oxygen levels in the foil bags and cans are assumed to be the principal reason for better preservation of coal samples in these containers.

Fluorescence

Alteration of vitrinite fluorescence intensity is measured with photometric readings taken at regular intervals during a period of constant irradiation with blue light. For freshly mined coal, alteration patterns change from positive in lignites to one showing a dual response (first decreasing then increasing) for high volatile coals and finally becoming negative in medium volatile coals. Recent work has shown that different mechanisms of photochemical oxidation may be responsible for the formation (positive alteration) and destruction (negative alteration) of fluorophoric sites during blue–light irradiation (8). When coal becomes weathered its pattern of alteration changes from dual to positive and the mean fluorescence intensity of vitrinite also decreases (9).

Fluorometric analysis of high volatile coals stored at –6 mm for more than 30 months shows that the positive component of alteration increases and mean fluorescence intensity (F_{1600}) decreases with time. However, the alteration pattern for the medium volatile Lower Kittanning coal in this study is unchanged after 49 weeks of storage, whereas intensity decreases significantly (10). Thus, fluorescence intensity is a more sensitive measure of short–term storage changes in the medium volatile coal than alteration.

Other Properties

The alkali extraction test for oxidation of bituminous coal was performed on all samples. According to this test, all containers of the Lower Kittanning sample allowed oxidation with a narrow range of results; –6 mm coal in foil bags was preserved best and the exposed sample fared worst. For the Argonne samples (Table 1), those repackaged in foil bags compared favorably to those in ampoules, but both readings tended to be lower than those on the original ampoules. The precision of this test has not yet been determined.

Total conversion and product yield were determined from tubing–bomb liquefaction experiments (350°C, 30 min, 1000 psig H_2, 2:1 tetralin to coal ratio) for samples stored for 4 and 16 weeks in foil laminate bags and 4 weeks in a polyethylene bucket. Although conversion ranged from 17.9 – 21.7% and oil yields from 2.5 – 3.3%, no significant difference attributable to storage methods was observed.

Selected samples were examined with FTIR; no significant differences in carbonyl (~ 1600 cm^{-1}) or aliphatic stretching (~ 2920 cm^{-1}) were found between the foil bag and bucket storage after 4 and 16 weeks.

DISCUSSION

Conventional storage containers can cause sample deterioration. Based on this study and the desire to improve sample preservation in long-term storage, samples collected since December, 1989 for the Penn State Coal Sample Bank are being stored in foil laminate bags after processing. At this time all such samples are designated DECS (Department of Energy Coal Samples).

For field collection and temporary storage prior to processing, steel barrels with high-density gaskets (11) are employed. Samples are processed into –6 mm and –0.85 mm mesh sizes. Coal crushed to –0.85 mm is stored as 300 g splits in 19 x 24 cm foil laminate bags, –6 mm material is stored in either 2 kg or 12 kg splits in larger bags (23 x 38 or 50 x 64 cm). This avoids the problem of poorer preservation of bulk samples caused by storage in a different container type.

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Table 1. Gieseler Fluidity and Alkali Extraction Data for Argonne Premium Coal Samples

	ANL-101, Upper Freeport, mvb			ANL-301, Illinois #6, hvBb		
Gieseler Fluidity	As Rec'd	Stored in Ampoule	Stored in foil bag	As Rec'd	Stored in Ampoule	Stored in foil bag
max. fluidity, ddpm	29,998	29,934	29,910	72	54	
initial fluidity T, °C	381	376	386	368	367	test
max. fluidity T, °C	456	456	454	418	413	failed
solidification T, °C	507	502	498	447	444	
fluid range, °C	126	126	112	79	77	
Alkali Extraction						
% transmittance	94.5	91.7	87.7	95.3	86.2	91.1

	ANL-401, Pittsburgh, hvAb			ANL-501, Pocahontas #3, lvb		
Gieseler Fluidity	As Rec'd	Stored in Ampoule	Stored in foil bag	As Rec'd	Stored in Ampoule	Stored in foil bag
max. fluidity, ddpm	25,055	17,093		46	39	37
initial fluidity T, °C	386	384	test	453	444	445
max. fluidity T, °C	438	430	failed	486	480	484
solidification T, °C	475	473		515	511	508
fluid range, °C	89	89		62	67	63
Alkali Extraction						
% transmittance	96.4	91.8	91.5	97.9	95.4	95.1

	ANL-601, Blind Canyon, hvBb			ANL-701, Lewiston-Stockton, hvAb		
Gieseler Fluidity	As Rec'd	Stored in Ampoule	Stored in foil bag	As Rec'd	Stored in Ampoule	Stored in foil bag
max. fluidity, ddpm	2	2		112	12	119
initial fluidity T, °C	404	398	test	410	406	409
max. fluidity T, °C	424	415	failed	445	422	437
solidification T, °C	446	438		469	431	463
fluid range, °C	41	40		59	25	54
Alkali Extraction						
% transmittance	96.0	89.9	87.6	95.7	81.7	90.9
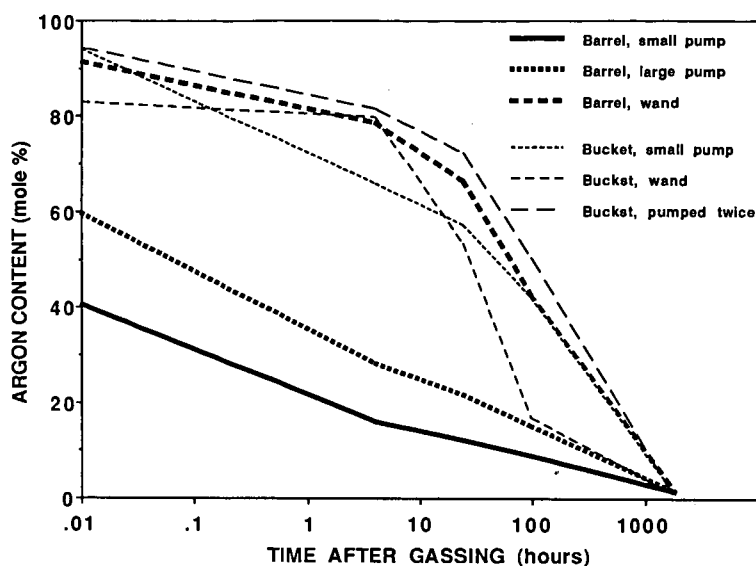
Figure 1. Argon in Barrel and Bucket Atmospheres

Legend:
- Barrel, small pump
- Barrel, large pump
- Barrel, wand
- Bucket, small pump
- Bucket, wand
- Bucket, pumped twice

Y-axis: ARGON CONTENT (mole %)
X-axis: TIME AFTER GASSING (hours)
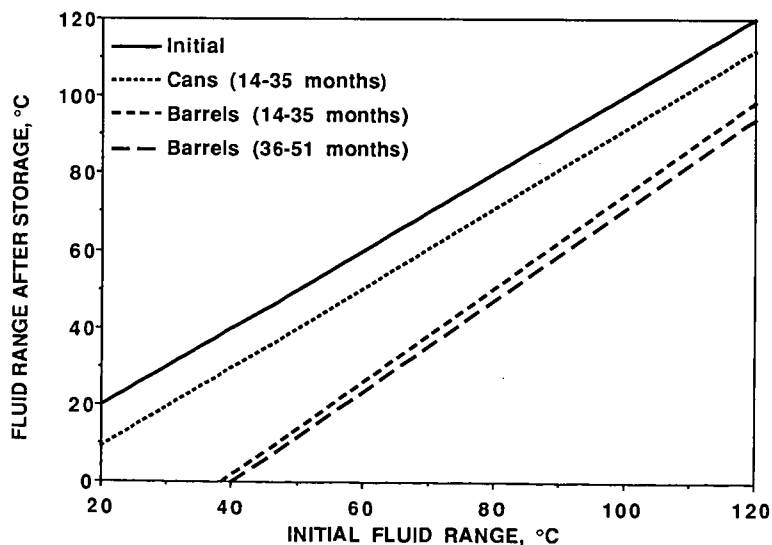
Figure 2. Gieseler Fluid Range: Linear Regression on 28 Samples

Legend:
- Initial
- Cans (14-35 months)
- Barrels (14-35 months)
- Barrels (36-51 months)

Y-axis: FLUID RANGE AFTER STORAGE, °C
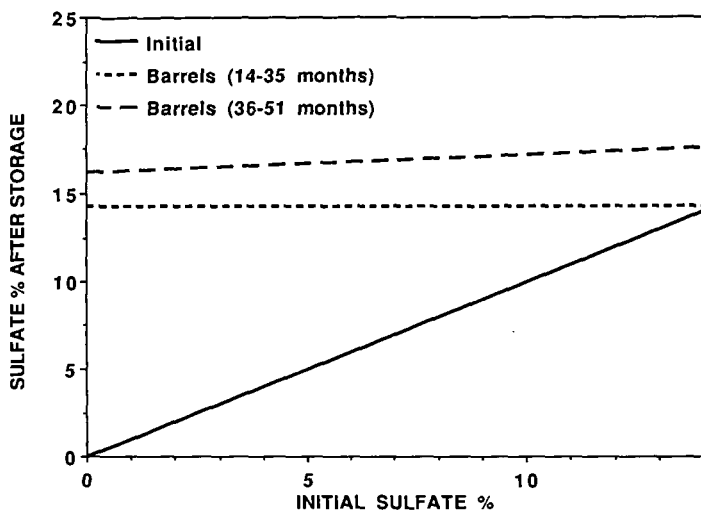X-axis: INITIAL FLUID RANGE, °C

Figure 3. Sulfate Sulfur as % of Total Sulfur: Linear Regression on 53 samples
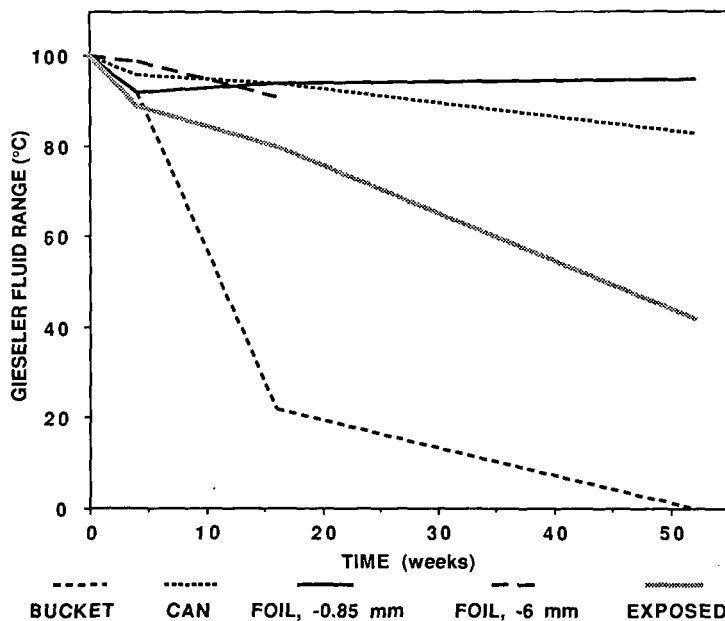

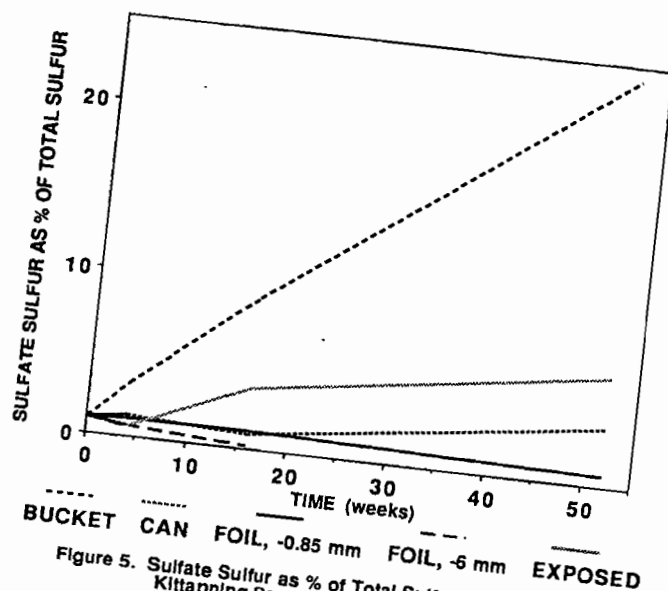Figure 4. Gieseler Fluid Range of mvb Lower Kittanning Seam Sample

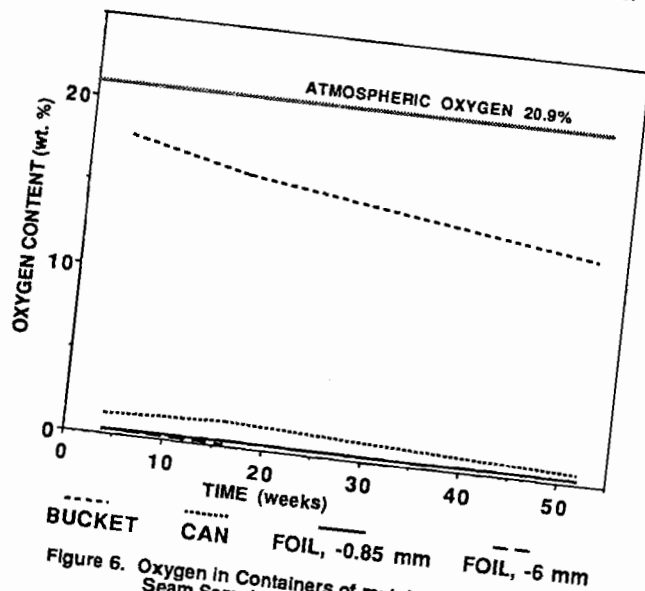Figure 5. Sulfate Sulfur as % of Total Sulfur in mvb Lower Kittanning Seam Sample

Figure 6. Oxygen in Containers of mvb Lower Kittanning Seam Sample

ORGANIC OXYGEN CONTENTS OF ARGONNE PREMIUM COAL SAMPLES

Bongjin Jung, Shawn J. Stachel, and William H. Calkins*
Center for Catalytic Science and Technology, Department of Chemical Engineering
University of Delaware, Newark, DE19716

Keywords: Organic Oxygen, Flash Pyrolysis, FNAA

ABSTRACT

The organic oxygen content has been determined for the Argonne premium coal samples through fast neutron activation analysis (FNAA) of the dry original coal and low temperature ash (LTA). This is compared with the oxygen-by-difference method using elemental analysis and high temperature ash corrected by the Parr Formula. The total organic oxygen content is compared with oxygen functional group contents as determined by chemical and flash pyrolysis techniques.

INTRODUCTION

The organic oxygen components of coal are important in determining coal structure and reactivity in coal liquefaction and other processes (1). Coal contains substantial amounts of chemically bound oxygen in the organic components in addition to the oxygen associated with mineral matter in coal. The total oxygen content decreases with the rank of the coal (2). The conventional ASTM method (3) used to estimate the organic oxygen content of coal is to subtract from 100 the sum of the percentages of carbon, hydrogen, nitrogen, sulfur, and high temperature ash. All errors in these determinations and errors due to large weight changes in the coal mineral matter in the ASTM high temperature ash method are included in the oxygen-by-difference estimate. This can be corrected to some degree by the modified Parr Formula (4), but the result is only an estimate.

Fast neutron activation analysis (FNAA) has been used to determine organic oxygen of coal directly by several workers (5,6,7). Low temperature ashing instead of ASTM high temperature ash method has been used with fast neutron activation analysis of the ash and the dried coal for the determination of organic oxygen (5,6). Mahajan (7) and others have reported that, during low temperature ashing of coals, mineral matter present in coal undergoes minimal change in composition. Organic oxygen is calculated from the following difference of FNAA determinations of total dry coal oxygen and oxygen in low temperature ash.

$$\% \ O_{organic} = \% \ O_{total} - \% \ O_{LTA} \times g \ LTA/g \ coal$$

The problems involved in determining the organic oxygen content of coal were discussed in detail by Given and Yarzab (8).

Oxygen structures in coal give off water, carbon monoxide or carbon dioxide on pyrolysis, and the temperatures at which these are evolved depend on the functional groups. Pyrolysis together with NMR and other analytical methods may allow us to identify the particular oxygen functional groups in the coal, and correlate this with process studies.

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*To whom communications should be sent

There is chemical evidence for the presence of hydroxyl, carbonyl, carboxyl, and methoxy groups in low-rank coals, and for hydroxyl and carbonyl groups in higher rank coals (9, 10). However a certain fraction of the oxygen is not detected by standard chemical analyses and is usually considered to be ether oxygen. It has been speculated that coal liquefaction consists at least in part in the cleavage of ether linkages between aromatic ring clusters (11, 12), leaving free radical ends which are capped by hydrogen transfer from coal or a donor solvent. Cleavage of ether groups might be expected to give more phenolic groups (13). The principal evidence for this is the presence of more phenolic groups after liquefaction than were present in the original coal (12, 14). However, the presence and type of ether groups in coal and the role of oxygen functionalities in coal liquefaction is still obscure (1).

It is to try to provide more information on the oxygen functional groups distribution and organic oxygen species in coal and their roles in coal processes that this work was undertaken. The research described will be an important step toward understanding the chemistry of the coal pyrolysis process. To the extent that it is successful in developing an understanding of coal structure it will also assist in developing an understanding of coal liquefaction and other coal conversion processes.

EXPERIMENTAL

Coals Studied

The eight coals from the Argonne premium coal sample program were studied (see Table 1).

Low Temperature Ashing

The low temperature asher (LFE Corp., LTA-302) was operated at around 75-100 W depending on fluctuations in the unit while running. The oxygen flow rate was kept at 100 cc/min. All the samples (approximately 0.2 g) were ashed after being ground under nitrogen for one hour with a mortar and pestle. The samples in the boat were stirred to expose fresh surface for oxidation approximately every 5 hours. Ashing was continued until constant weight of the sample was obtained. All of the low temperature ash samples were sealed in air tight vials in the nitrogen atmosphere of a glove box. In the case of Wyodak and Beulah samples the low temperature ash was measured on both the original and acid forms.

Chemical Methods

The chemical methods of Blom and Schafer (9, 10) were used for analysis of the oxygen functional groups in coal such as carboxyl, hydroxyl, and carbonyl. Ethers (internal and external) were estimated by difference. Kjeldahl nitrogen runs as part of the carbonyl determination were run by Micro Analysis Inc.

Pyrolysis Method

The pyrolysis experiments were conducted on the Beulah-Zap and Wyodak samples at 625-930°C with 74-105 μm fractions in a continuous fluidized sand bed pyrolyzer (described in detail in reference 15). The coals used were ground in a SPEX mill or mortar and pestle in a nitrogen atmosphere, sieved, and then vacuum dried at 104-107°C for approximately 20 hours. The coal particles were entrained into a nitrogen stream in the coal feeder and carried over into the fluidized sand bed at various flash pyrolysis temperatures.

The coal feeder was suspended from a Mettler balance and the change in its weight with time was monitored by a Linseis recorder. Coal was fed at uniform rates of 0.03-0.1 grams/min and approximately 1-2 grams total are fed. Upon entering the pyrolyzer, the coal was rapidly heated to the bed temperature at a rate of approximately 10^4 °C/sec and residence time (assuming full utilization of the expanded fluidized sand bed) was about 0.5 sec. Thermocouple wells in the reactor allow close monitoring of the temperature in the reactor bed and in the region above it. The pyrolysis products exit the pyrolyzer to a set of three cold traps. A side stream after the first trap can be vented to a Panametrics hygrometer for measurement of water content. The gases were collected and analyzed for CO and CO_2 in a Perkin-Elmer Sigma 1B gas chromatograph. The tars were collected in Soxhlet thimbles for later recovery by Soxhlet extraction with methylene chloride and subsequent analysis in an HP5880A gas chromatograph/mass spectrometer.

RESULTS AND DISCUSSION

Organic Oxygen Content: We have run eight Argonne National Laboratory (ANL) premium coal samples in the low temperature asher. The remaining ash, after the sample reached constant weight, was analyzed by Radioanalytical Services of the University of Kentucky for determination of percent oxygen through fast neutron activation. This value was subtracted from the total oxygen content, which was determined in the same manner on the dried coal itself, to give the percent organic oxygen for each sample of coal. Oxygen values reported by FNAA are for at least three replicate analyses of the same sample. The oxygen contents of eight coals and their low temperature ashes are shown in Table 1. A comparison of % low temperature ash of the samples between our experiments and ANL data (16) are generally in close agreement, except for the Beulah-Zap and Wyodak samples which are somewhat higher in this study. The reason for this difference is not apparent. The organic oxygen contents of the dried coals determined by FNAA method are compared in Table 2 with those determined by oxygen-by-difference using elemental analysis and high temperature ash corrected by the Parr Formula. These two values are generally in agreement. Table 3 shows the elemental analysis of samples (16) by direct determination including the contents of low temperature ashes and the total organic oxygen determined by FNAA method. It will be noted that the total of these values are approximate 100 %, except for the Illinois #6 coal which is somewhat high. The reason for this is being investigated.

Low-rank coals contain the large concentration of exchangeable metal ions associated with the carboxyl groups. In the case of Wyodak and Beulah-Zap samples, the comparison of % low temperature ash of the original and acid forms show significant concentrations of associated metal ions, as shown in Table 4.

Chemical Methods: The percent oxygen as carboxyl, hydroxyl, carbonyl, and ether (by difference) in each sample is shown in Table 5. Carboxylic groups are found in considerable concentration in the low-rank coals. The percent oxygen in carboxyl groups decreases with increasing rank and approaches zero for coals of higher rank. The percent oxygen as hydroxyl and carbonyl show similar trend with increasing rank, but carbonyl shows greater variability. There is significant amounts of ether oxygen (by difference) in all samples. Illinois #6 coal, however, seems to be somewhat lower in ether oxygen than might be expected for its rank.

Flash Pyrolysis: The pyrolysis of coal over a range of controlled conditions offers a possible unexploited and independent approach to studying the oxygen species in coal. The structural interpretations of pyrolysis data of coal sample are compared to total organic oxygen contents determined by FNAA and oxygen functional group contents such

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as % carboxyl, % hydroxyl, % carbonyl, and % ether (by difference) by chemical methods.

The corresponding oxygen yields of Wyodak subbituminous as a function of pyrolysis temperature are shown in Figure 1. The main oxygen-containing products of the decomposition of oxygen groups of the sample are H_2O, CO_2, and CO. Some water is adsorbed in coal and some may appear through decomposition of chemical structures. Carboxyl content as determined by CO_2 evolution agrees closely with chemical analysis indicating that carboxyl groups pyrolyze quantitatively to CO_2 (17). Water and CO_2 evolution occurs below 700 °C.

CO is a major gaseous product of coal pyrolysis and oxygen yield as CO continues increasing with temperature up to 930 °C. More experimental work is need to confirm the carbon monoxide emissions at temperatures in the range of 950-1000 °C. Based on model compounds studied, hydroxyl and ether groups appear to evolve mainly carbon monoxide and possibly water. Very preliminary work by one of the writers (15) at temperatures in the range of 600-1000 °C tend to confirm those observations and suggest that in our system these carbon oxide emissions may be complete and reasonably quantitative by 950-1000 °C.

Total oxygen yield from oxygen-containing groups increased with temperature. The total organic oxygen contents of the sample determined by flash pyrolysis technique and fast neutron activation analysis are in fairly close agreement.

CONCLUSIONS

The conclusions of this work are as follows

1. The organic oxygen contents of the dried coals determined both by FNAA method and by oxygen-by-difference using the modified Parr Formula on high temperature ash are generally in agreement.

2. The percent carboxyl, hydroxyl, and carbonyl groups of samples decrease with increasing rank. Ethers represent a significant fraction of the organic oxygen in the Argonne coals.

3. Temperatures approaching 1000 °C are required to pyrolyze all the oxygen groups in coal.

4. Carboxyl groups in coal pyrolyze quantitatively to CO_2 below 700 °C.

5. A substantial proportion of the mineral matter in low-rank coals is associated with the carboxyl groups.

ACKNOWLEDGMENTS

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Table 1. Organic Oxygen Contents of Argonne Premium Coal Samples (dry, wt %) by Fast Neutron Activation Analysis

Coal	Beulah-Zap	Wyodak-Anderson	Illinois #6	Blind Canyon	Pittsburgh #8	Lewiston-Stockton	Upper Freeport	Pocahontas #3
Rank	Lig.	Subb.	HVB.	HVB.	HVB.	HVB.	MVB.	LVB.
C(dmmf)	74.05	76.04	80.73	81.32	84.95	85.47	88.08	91.81
LTA by ANL	8.7	8.7	18.1	5.3	10.9	21.6	15.3	5.5
LTA^a	11.88	11.51	19.77	5.7	10.05	21.9	15.7	5.8
O_{LTA}^b	51.3	55.5	37.9	48.0	41.4	49.1	38.4	45.4
O_T^c	23.3	20.7	14.9	12.5	10.9	16.5	8.93	4.22
O_{org}^d	17.2	14.31	7.41	9.76	6.74	5.75	2.90	1.59

[a] Low temperature ash in this study

[b] Oxygen content of low temperature ash by FNAA

[c] Total oxygen content of coal by FNAA

[d] Organic oxygen content of coal by % $O_{organic}$ = % O_{total} - % O_{LTA} x g LTA/g coal

Table 2. Comparison of Organic Oxygen Contents of Argonne Premium Coal Samples (dry, wt %) by Fast Neutron Activation Analysis and Oxygen-by-Difference Methods

Coal	Beulah-Zap	Wyodak-Anderson	Illinois #6	Blind Canyon	Pittsburgh #8	Lewiston-Stockton	Upper Freeport	Pocahontas #3
Rank	Lig.	Subb.	HVB.	HVB.	HVB.	HVB.	MVB.	LVB.
C(dmmf)	74.05	76.04	80.73	81.32	84.95	85.47	88.08	91.81
ANL^a O_{org}^b	17.01	15.21	8.21	10.29	6.13	5.17	3.98	1.57
$Exp.^c$ O_{org}^d	17.21	14.31	7.41	9.76	6.74	5.75	2.90	1.59

[a] Argonne National Laboratory

[b] Organic oxygen content of coal by difference using elemental analysis and high temperature ash % corrected by Parr Formula

[c] Our experimental data by FNAA

[d] Organic oxygen content of coal by % $O_{organic}$ = % O_{total} - % O_{LTA} x g LTA/g coal

Table 3. Elemental Analysis by Direct Determination of Argonne
Premium Coal Samples (dry, wt %)

Coal	Beulah-Zap	Wyodak-Anderson	Illinois #6	Blind Canyon	Pittsburgh #8	Lewiston-Stockton	Upper Freeport	Pocahontas #3
Rank	Lig.	Subb.	HVB.	HVB.	HVB.	HVB.	MVB.	LVB.
C(dmmf)	74.05	76.04	80.73	81.32	84.95	85.47	88.08	- 91.81
C[a]	65.85	68.43	65.65	76.89	75.50	66.20	74.23	86.71
H[a]	4.36	4.88	4.23	5.49	4.83	4.21	4.08	4.23
N[a]	1.04	1.02	1.16	1.50	1.49	1.25	1.35	1.27
S[a]	0.80	0.63	4.83	0.62	2.19	0.71	2.32	0.66
Cl[a]	0.04	0.03	0.05	0.03	0.11	0.10	0.00	0.19
F[a]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O_{org}[b]	17.21	14.31	7.41	9.76	6.74	5.75	2.90	1.59
LTA[c]	11.88	11.51	19.77	5.7	10.05	21.9	15.7	5.8
Total	101.18	100.81	103.10	99.99	100.91	100.12	100.58	100.45

[a] Data from ANL user handbook

[b] Organic oxygen content of coal by % $O_{organic}$ = % O_{total} - % O_{LTA} x g LTA/g coal

[c] Low temperature ash in this study

Table 4. Metal Ions Associated with Low-Rank Coals

Coal	Beulah-Zap (wt %)	Wyodak-Anderson (wt %)
Low Temperature Ash on Raw Coal	11.88	11.51
Low Temperature Ash on Acid Form	2.87	5.7
Associated Metal Ions	9.01	5.81

Table 5. Determination of Organic Oxygen Contents by Chemical and Pyrolytic Analyses of Argonne Premium Coal Samples (dry, wt. %)

| Coal	Beulah-Zap	Wyodak-Anderson	Illinois # 6	Blind Canyon	Pittsburgh # 8	Lewiston-Stockton	Upper Freeport	Pocahontas # 3
Rank	Lig.	Subb.	HVB.	HVB.	HVB.	HVB.	MVB.	LVB.
C(dmmf)	74.05	76.04	80.73	81.32	84.95	85.47	88.08	91.81
Total Organic O by FNAA (1)	17.21	14.31	7.41	9.76	6.74	5.75	2.90	1.59
% O as CO_2H by Chemical Method (2)	3.81	3.33	0.23	0.23	0.16	0.20	0.14	0.05
% O as CO_2H by Pyrolysis Method	3.94	3.14						
% O as OH by Chemical Method (3)	9.16	7.68	5.68	5.22	4.32	2.70	1.96	0.98
% O as C=O by Chemical Method (4)	1.96	0.74	0.93	0.63	0.18	0.18	0.44	0.32
% O as Ether by Difference (1) - (2) - (3) - (4)	2.28	2.56	0.57	3.68	2.08	2.67	0.36	0.24
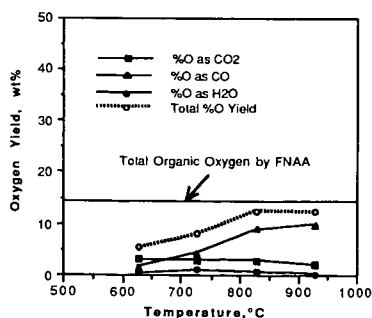
Figure 1. Oxygen Yield from Pyrolysis of Wyodak Subbituminous Coal in Fluidized Bed Pyrolyzer

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QUANTITATIVE ^{13}C NMR MEASUREMENTS ON THE ARGONNE PREMIUM SAMPLES AND OTHER COALS

Colin E. Snape and Gordon D. Love
University of Strathclyde, Dept. of Pure & Applied Chemistry,
Thomas Graham Building, 295 Cathedral St., Glasgow G1 1XL, UK

ABSTRACT

In view of the well-documented inherent problems with cross-polarisation (CP) ^{13}C NMR concerning quantification for coals, the more time-consuming single pulse excitation (SPE) or Bloch decay technique has much to commend it. SPE ^{13}C NMR has been carried out on the Argonne Premium Samples and a selection of UK coals and maceral concentrates at a low field strength (25MHz) to avoid problems with spinning sidebands. In addition to aromaticity measurements, quaternary aromatic carbon concentrations have been determined by SPE dipolar dephasing. As anticipated, much greater proportions of the carbon were obseved by SPE than by CP and the use of tetrakis(trimethylsilyl)silane as an internal standard has indicated that over 90% of the carbon in most of the coals is observed by SPE. Moreover, aromaticity values measured by SPE are consistently higher than those from CP. For anthracite, the concentration of bridgehead aromatic carbon measured by dipolar dephasing SPE is in close agreement with that from elemental analysis.

INTRODUCTION

The combination of dipolar decoupling and magic angle spinning (MAS) with cross-polarisation now enables ^{13}C NMR spectra of carbonaceous materials to be obtained on a routine basis. Although ^{13}C NMR has shown considerable potential for the characterisation of coals, oil shales and other humic materials [1,2], there has been considerable doubt concerning the quantitative reliability of aromaticity and other skeletal parameter measurements using this technique [3]. There is a consensus that significant errors can arise in CP/MAS ^{13}C NMR measurements of aromaticity and other skeletal parameters due to the unfortunate spin-dynamics of carbonaceous materials which typically result in only 50% of the carbon being observed for bituminous coals. Although it is well established that the rate of magnetisation transfer from abundant ^{1}H to dilute ^{13}C spins during CP is slower for quaternary aromatic carbons than for protonated carbons, the major problem for coals is undoubtedly the presence of paramagnetic species which cause ^{1}H spins to relax too quickly during CP, i.e. before polarisation transfer to ^{13}C spins has been achieved. In addition, carbons in the vacinity of paramagnetic centres are not observed due to a combination of shielding effects and rapid relaxation. Thus, in general, there is often a clear discrimination against aromatic carbon . Moreover, additional problems are posed by measurements at high field strengths where either much higher spinning speeds or special pulse sequences (e.g. TOSS) are needed to remove sidebands associated with aromatic peaks.

In view of the well-documented inherent problems with CP ^{13}C NMR concerning quantification for solid fuels [2,3], the use of the more time-consuming Bloch decay or single pulse excitation (SPE) technique has much to commend it, particularly at low field strengths to avoid problems with spinning sidebands. This paper covers the application of SPE ^{13}C NMR to the Argonne Premium Coal Samples, a number of UK coals and maceral concentrates, the results being compared with those reported here and by other workers from CP. In addition to aromaticity measurements, dipolar dephasing has been used with SPE to estimate the quaternary aromatic carbon concentration in an anthracite.

EXPERIMENTAL

All the Argonne Premium Coal Samples were analysed except Pocahontas. The 3 UK bituminous coals investigated where Linby, Gedling (both 83% dmmf C) and Point of Ayr (87% dmmf C),

together with an anthracite (Cynheidre). The maceral concentrates were obtained from a US Kentucky low volatile bituminous coal (88% dmmf C) by density gradient centifugation.

Most of the measurements were carried out at 25MHz on a Bruker MSL100 spectrometer with MAS at 4.5 kHz to give virtually sideband free spectra. For CP, contact times were varied between 0.1 and 15 ms. A relaxation delay of 20s was used in SPE in view of the fact that the few published values of ^{13}C thermal relaxation times for coals are at least 5s [4-6]. No background signal was evident in the SPE spectra from the Kel-F rotor caps. Typically, between 3000 and 4000 scans were accumulated for both the CP and SPE spectra. Dipolar dephasing was carried out with both variable and fixed (50us) dephasing periods. Some spectra were also obtained at high field (75 MHz) with rapid MAS (>10 kHz) using a Varian VXR300 spectrometer. Tetrakis(trimethyl)silane (TKS) was used as an internal standard to determine the proportions of carbon observed in the samples investigated. In experiments with TKS, the acquisition time was extended from 30 to 250 ms to avoid truncating the free induction decay.

RESULTS AND DISCUSSION

Figure 1 shows the 25 MHz SPE spectra of N.Dakota lignite, Pittsburgh No.8 coal and Cynheidre anthracite and indicates that the signal to noise levels are high (50 Hz line broadening routinely used). Moreover, the intensities of the sidebands are below 5% of the central aromatic peaks with MAS at 5 kHz. The 25 MHz SPE and CP spectra of one of the bituminous coals (Gedling) are shown in Figure I and it is evident that significantly more aromatic carbon is observed by SPE. Table 1 compares the aromaticity values derived by SPE and CP for the coals investigated and the same trend is found in most cases. Indeed, differences in the measured aromaticity values by the two methods range from 3 to 10 mole%. For CP, the differences are small between the values obtained with a contact time of 1ms and those obtained by fitting the intensities of the aromatic and aliphatic bands from multiple contact experiments to the form.

$$I_o = I_t \exp(1-t/T_{CH}).\exp(-t/T_{1\rho})$$

where T_{CH} is the time constant for CP and $T_{1\rho}$ is the ^{1}H rotating frame relaxation time.

For the Argonne samples, the CP-determined aromaticities are generally in reasonable agreement ($\pm$ 2 mole %) with those reported by Botto and Axelson [5] and Pugmire et al [7]. However, at relatively long contact times (>4 ms), the values obtained were typically 2-3% higher than those from using a contact time of 1ms and multiple contacts (Table 1). Illinois No.6, Pittsburgh No.8, Lewiston-Stockton, Linby, Gedling and Point of Ayr coals all have H/C ratios between 0.76 and 0.78 despite their carbon contents varying between 80 and 87%. Interestingly, their 25 MHz SPE-determined aromaticities fall in the relatively narrow range of 0.77-0.81. Indeed, one of the authors has argued previously that such aromaticities are more consistent with the H/C ratios than the considerably lower CP-determined values of 0.72±0.04 (Table 1). Of the coals investigated, the lowest proportion of the carbon was observed by SPE for Upper Freeport coal (80%, Table 1) and, with the exception of the anthracite, this was the only coal for which CP and SPE gave the same aromaticity value within the experimental error of about ±1%. From the H/C ratio of 0.67 for this coal and the SPE-determined aromaticities discussed above, a value close to 0.85 would have been anticipated. Indeed, if it is assumed that the 20% of the carbon not observed is aromatic, then the measured value of 0.81 increases to 0.84. Although aromaticities derived from the high-field SPE spectra (Figure 3 shows the 75 MHz spectrum for Linby coal) were less precise due to a combination of the greater sideband intensities, the high-field sidebands overlapping with the aliphatic bands and some background signal being obtained from the Kel-F rotor caps, reasonable agreement was obtained with values from the low-field spectra (Table 1).

Figure 4 shows the SPE spectra for the liptinite, vitrinite and inertinite concentrates and, as anticipated, aromaticity increases in going from liptinite to vitrinite to inertinite. However, as for the whole coals, the respective aromaticity values of 0.60, 0.80 and 0.89 are considerably higher than those determined by CP and over 85% of the carbon was observed.

The concentration of quaternary aromatic carbon was estimated by dipolar dephasing using both CP and SPE for the anthracite. Figures 5 and 6 present the decays of the aromatic carbon intensities with increasing dephasing time for CP (10 ms contact time) and SPE, respectively; it was expedient to obtain

more data points for CP because of the superior signal to noise ratios obtained with the much shorter recycle times. Figure 5, in particular, indicates the modulation of the decaying aromatic peak by the MAS. However, in both plots, the expected two component decay is observed. As anticipated with a relatively short contact time (1 ms), the value obtained of about 50 mole % quaternary aromatic carbon was considerably lower than that of 0.67 from the H/C ratio and the SPE-determined aromaticity. Considerably higher values of 67 and 69 mole % C were obtained from Figures 5 and 6 for long contact time CP and SPE, respectively. Moreover, these values are in close agreement with the estimate discussed above from elemental analysis. It should be pointed out that the anthracite investigated here has a slightly higher atomic H/C ratio than that investigated by Gerstein and co-workers [8] and this is consistent with the value obtained with a contact time of 1 ms (50%) being lower than that of about 65% reported in Gerstein's study with a similar contact period. The dipolar dephasing SPE experiment is being extended to the other coals and also being used to estimate methyl concentrations.

CONCLUSIONS

The results clearly demonstrate that, for most coals, aromaticity and other skeletal parameters measured by SPE ^{13}C NMR are quantitatively reliable with typically over 90% of the carbon being observed. The SPE-determined aromaticities of high volatile bituminous coals having H/C ratios of about 0.78 are close to 0.8 and these values are consistently higher than those in the range 0.68-0.75 measured by CP. The development of larger rotors for MAS [6] will help make SPE measurements an even more attractive proposition for quantitative ^{13}C NMR analysis of solid fuels.

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ACKNOWLEDGEMENTS

Table 1 Aromaticity values derived from the 25 MHz spectra of the coals

Sample	% dmmf C	Aromaticity values				% of carbon observed by SPE
		CP-1ms	CP-7ms	CP-fit	SPE	
N.Dakota lignite	73	0.66	0.69	0.65 (0.65)	0.76	94
Wyodak sub-bit.	75	0.62	0.65	0.63 (0.63)	0.75	100
Illinois No.6	80	0.70	0.73	0.70 (0.72)	0.78 [0.76]	92
Pittsburgh No.8	83	0.72	0.73	0.72 (0.72)	0.77	89
Blind Canyon	81	0.62	0.62	0.63 (0.63)	0.65	96
Linby	83	0.68	0.72	0.68 (0.68)	0.81 [0.79]	100
Gedling	83	0.68	0.74	0.67 (0.67)	0.78	95
Lewis.-Stockton	84	0.69	n.d.	n.d.	0.79	100
Point of Ayr	87	0.71	0.75	0.71	0.79	92
Upper Freeport	88	0.75	0.79	0.77 (0.80)	0.81	83
Cynheidre anthracite	95	0.96	0.98	0.96 (0.98)	0.99	94

CP-fit = from multiple contact experiments, ( ) = values from fitting aromatic carbon band to two components for T_{CH} and $T_{1\rho}$ which gave much better fits.

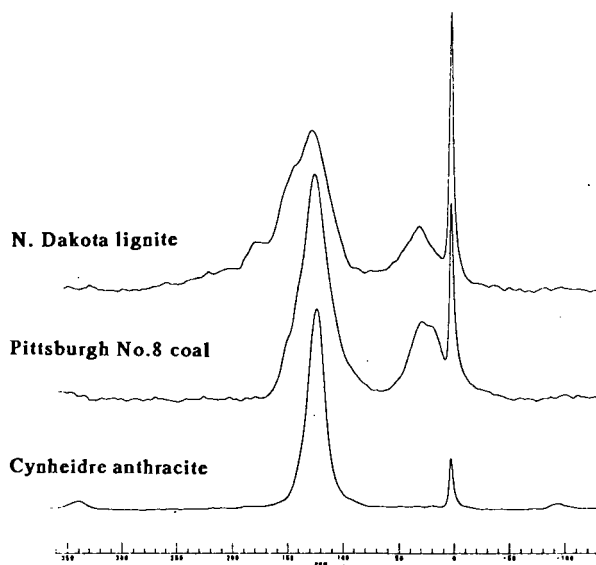[ ] = values from 75 MHz spectra.   n.d. = not determined.

N. Dakota lignite

Pittsburgh No.8 coal

Cynheidre anthracite

FIGURE 1 25 MHz SPE ^{13}C NMR SPECTRA OF SOME OF THE COALS

CP

SPE
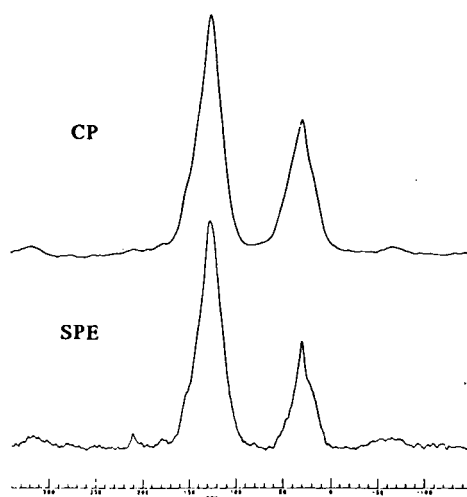
FIGURE 2 25 MHz CP AND SPE ^{13}C NMR SPECTRA OF GEDLING COAL

881

FIGURE 3 75MHz SPE SPECTRUM OF ILLINOIS No. 6 COAL

FIGURE 4 25 MHz SPE SPECTRA OF MACERAL CONCENTRATES

882

Ln % aromatic intensity

Dephasing time us
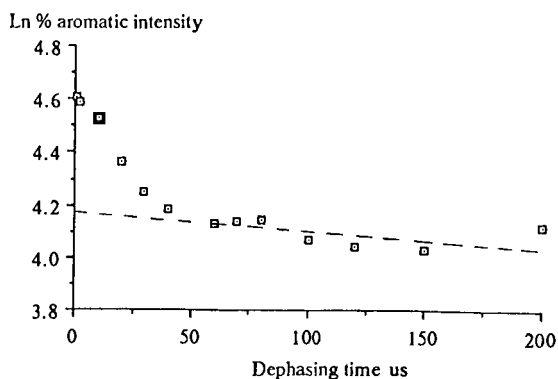
FIGURE 5 AROMATIC CARBON INTENSTIES FROM CP DIPOLAR DEPHASING EXPERIMENT ON THE ANTHRACITE

Ln % aromatic intensity
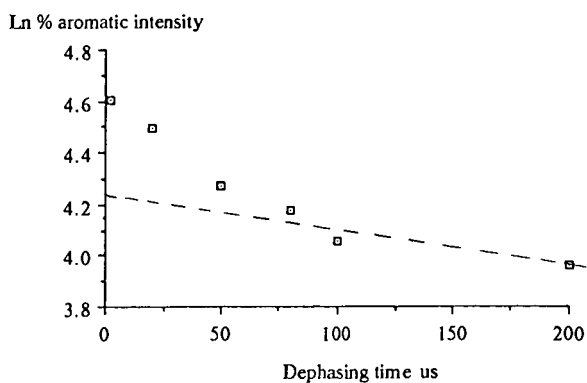

Dephasing time us

FIGURE 6 AROMATIC CARBON INTENSITIES FROM SPE DIPOLAR DEPHASING EXPERIMENT ON THE ANTHRACITE

HYDROGEN TRANSFER FROM NAPHTHENES TO COAL DURING COPROCESSING

Ruth M. Owens and Christine W. Curtis
Chemical Engineering Department
Auburn University, Alabama 36830

Abstract

Hydrogen transfer from naphthenes to aromatics, coal, resid, and coal plus resid has been investigated at 430°C in a N_2 atmosphere. The reaction of perhydropyrene (PHP) with anthracene (ANT) resulted in the formation of pyrene (PYR) and dihydroanthracene (DHA). The weight percents of the products formed varied according to the ratio of ANT/PHP with a minimum appearing at a 2 to 1 weight ratio. Increased reaction times and high ANT/PHP ratios also yielded tetrahydroanthracene (THA). Reactions of Illinois No. 6 coal from the Argonne Premium Coal Bank with PHP, ANT, and PYR resulted in higher coal conversion with PHP and lower with ANT and PYR. With PHP less retrogressive reactions occurred in the resid than with either PYR or ANT. Apparent hydrogen transfer from coal or resid to ANT and PYR was observed. Combining PHP with ANT or PYR with coal, resid or coal plus resid yielded in higher conversions and less retrogressive reactions. Hydrogen transfer occurred from PHP to ANT or PYR and to the coal and resid as evinced by the increased conversion.

Introduction

The coprocessing of coal with petroleum residuum involves the simultaneous conversion of coal to liquid products and the upgrading of resid to higher quality products. These two feedstocks are quite different in composition with petroleum resid being hydrogen-rich with a hydrogen to carbon (H/C) ratio in the range of 1.4 to 1.6 while coal is hydrogen deficient with a H/C ratio of 0.6 to 0.8. The conversion of coal and the subsequent upgrading of coal liquids requires the transfer of hydrogen to coal. Many different sources of hydrogen are available to coal during typical coprocessing: hydrogen from hydrogen rich portions of the coal, hydrogen from aliphatic, naphthenic or hydroaromatic components in the resid, or hydrogen from the molecular hydrogen present in the reactor. Hydrogen from naphthenic components in the resid would provide a valuable hydrogen resource for coal and alleviate some dependence on molecular hydrogen.

This research investigates the hydrogen transfer from naphthene type structures in the resid to hydrogen acceptors: aromatic species, coal, and the resid itself. Previous research by Clarke et al. (Fuel, 63, 1476, 1984) had pointed to the possibility that hydrogen transfer was occurring between naphthenic components and coal resulting in increased conversion of coal and formation of aromatics from the naphthenes. In this work, a systematic set of experiments was performed using the naphthene perhydropyrene (PHP) reacted with the aromatic pyrene (PYR) or anthracene (ANT) to evaluate hydrogen transfer from naphthenes to aromatics in an inert atmosphere. Reactions were then performed with both naphthenes and aromatics with Illinois No. 6 coal from the Argonne Premium Coal Bank and with Maya resid individually and with the coal and resid combinatorially. Hydrogen transfer from both the naphthene to the coal and resid and from the coal and resid to the aromatic was examined.

Experimental

Materials. The chemicals used in this study included pyrene, perhydropyrene, and anthracene which were obtained from Aldrich Chemical at a purity of 99% or higher. The coal used was Illinois No. 6 from the Argonne National Laboratory Premium Coal Sample Program. The residuum used was Maya Resid from Amoco. The solvents used for the extraction analyses were toluene and THF from Fisher Scientific.

Procedure. Model compound and coprocessing reactions were conducted in small tabular microreactors charged with nitrogen gas. The reaction conditions for the model reactions were temperature of 430°C, N_2 at 400 psig ambient, and reaction times of 60, 90 and 180 minutes. For the single component model reactants, 0.1 gram was charged. For the binary component model reactants, the amount of individual reactant used ranged from 0.1 to 0.6g with the total amount of reactant charged ranging from 0.4 to 1.0g. Following the reaction the products were extracted with THF and analyzed by gas chromatography. The gaseous products from the reaction were analyzed using a Varian 3700 gas chromatograph equipped with a thermal conductivity detector and a molecular sieve column. The liquid products were analyzed on a Varian 3400 gas chromatograph using a HT-5 fused silica column from SGE and FID detection. The internal standard method with biphenyl as the internal standard was used for quantitation. Identification of the products was accomplished by GC mass spectrometry using a VG 70 EHF spectrometer.

The reactions containing coal and/or resid with model naphthene, aromatic or both were reacted at the same conditions as the model reactions except the reactions were conducted for 60 minutes only. Each reactant was charged at a level of one gram. After reaction the liquid and solid products were extracted with toluene to yield toluene solubles and with THF to yield THF solubles and insoluble organic matter (IOM).

Results and Discussion

Hydrogen Transfer in Thermal Coprocessing. A systematic set of experiments has been performed in our laboratory to evaluate whether hydrogen can be transferred directly from saturated naphthenes to coal and resid. The experiment performed evaluated the hydrogen transfer from naphthenic PHP to aromatics ANT or PYR. Reactions were then conducted to react PHP with Illinois No. 6 coal from the Argonne Premium Coal Bank, aromatics, ANT and PYR, with coal, and the combined system of naphthene and aromatic with coal. The same set of reactions was performed with Maya Resid: naphthene with resid, aromatics with resid, and naphthene and aromatic with resid. The final set that was performed involved naphthene, aromatic, coal and resid. Blank reactions were also performed with each individual material to evaluate the effect of the reaction conditions on the reactivity of the individual materials.

Hydrogen Transfer in the Model Reactions. The model systems that were used included the binary combinations of ANT with PHP and PYR with PHP. When reacted individually each of these reactants yielded no conversion. However, when reacted in combination the reactions involving ANT with PHP resulted in hydrogen transfer while no evidence of hydrogen transfer or any reactivity was observed with the PHP and PYR system.

The initial ANT and PHP reaction was performed with a 1 to 1 ratio of ANT to PHP. When reactivity was observed as the production of the partially saturated ·DHA and the formation of the unsaturated PYR, it was evident that hydrogen transfer had occurred since the only hydrogen available

was from PHP and that this reactive system should be further investigated. Three sets of experiments were performed at 60, 90 and 180 minutes with weight ratios of ANT to PHP ranging from 0.14 to ~ 10. Representative data are given in Table 1. Hydrogen transfer occurred at all of these conditions as evinced by the products formed. At 60 minute reaction time, DHA was formed at low ratios of ANT to PHP but decreased by two-thirds at an ANT/PHP weight ratio of 2 to 1. The weight ratio of DHA increased somewhat at higher ANT/PHP ratios as the production of tetrahydroanthracene (THA) began to be observed. At longer reaction times THA appeared at lower ANT to PHP weight ratios and more was formed. PYR was formed also during these reactions. The amount of PYR formed increased almost linearly with increasing ANT to PHP ratios. At the higher ANT to PHP ratios, the hydrogen donor PHP was limited while ANT was available in excess.

Given also in Table 1 are the percent hydrogenation (% HYD) and the hydrogen efficiency for these reactions. Percent HYD is defined as the moles of hydrogen needed to produce the liquid products as a percentage of those required to produce the most hydrogenated product, THA. Hydrogen efficiency is defined as the number of moles of hydrogen accepted to form a partially saturated species divided by the moles of hydrogen donated times 100%. Although some scatter appeared in these data, the % HYD appeared to the lowest and highest at low and high ratios of ANT to PHP. Hydrogen efficiency usually ranged from low to high with a minimum being present at a 2 to 1 ANT to PHP ratio. Higher hydrogen efficiencies were observed at higher ANT to PHP ratios where the stoichiometric weight ratio was approximately 6.3 to 1.

The data presented in Table 1 indicate that hydrogen transfer occurred under these conditions, albeit only a small amount of the naphthene and aromatic species reacted. These results strongly suggest that under certain reaction conditions hydrogen transfer can occur from naphthenes to aromatic species. This result may have important implications for coprocessing where a substantial portion of the resid solvent is composed of naphthenic structures and coal is composed of aromatic species.

Hydrogen Transfer in Coal and Resid Reactions. Hydrogen transfer between naphthenes and aromatics was evaluated in the presence of coal and resid individually and combinatorially. As with the model studies, all of the reactions were performed thermally in an inert atmosphere so that hydrogen transfer occurred only as a result of interactions among the reactants.

For this study, coal conversion is defined as moisture and ash free (maf) coal minus IOM divided by maf coal charged and multiplied by 100. The resid conversion or that portion of the resid remaining THF soluble is defined as the resid minus IOM divided by the resid charged and multiplied by 100. The coal and resid conversion is defined as maf coal plus resid minus IOM divided by maf coal and resid charged and multiplied by 100. The liquid to solid ratio is defined as the amount of toluene solubles divided by the amount of toluene insolubles present. Another term describing the degree of upgrading or degrading of the system in terms of the amount of toluene solubles was defined in order to provide a comparison among the different reactions with coal, resid, and coal plus resid. The degree of upgrading (TSD) is defined as the TOL solubles in the product minus the TOL solubles in the reactant divided by the upgradable materials. The upgradable materials are defined as maf coal for the coal reactions, resid for resid reactions and coal plus resid for the combined reaction. A positive number indicates that upgrading occurred while a negative number indicates retrogressive reactions.

Twelve different reaction systems were employed to evaluate hydrogen transfer between naphthenes and aromatics as shown in Tables 2 and 3. In addition, Illinois No. 6 coal and Maya resid were reacted individually to generate a baseline for their individual conversion and stability.

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The binary coal systems ranked in reactivity as coal/PHP > coal/PYR > coal/ANT. The reaction of coal with PHP resulted in the highest coal conversion as compared to the coal systems with ANT and PYR. Neither ANT or PYR promoted coal conversion. In fact, ANT increased the amount of IOM present substantially, yielding very low coal conversion, less than the coal by itself, while coal/PYR system yielded a conversion that was only slightly higher than coal by itself. The substantial increase in coal conversion in the coal/PHP system resulted in part from hydrogen transfer since PYR should have a higher solvating power for coal than PHP and higher conversion was obtained with PHP than PYR. Also, some PYR was produced indicating that dehydrogenation of PHP occurred as given in Table 3. Production of DHA and THA in the coal/ANT system indicated that hydrogen was transferred from coal to ANT.

Comparison of the ternary systems showed higher coal conversion for the system of coal/PHP/PYR than for coal/PHP/ANT, although little difference was observed in their toluene soluble yields. The effect of ANT in the system may be resultant from a lower solvating power for coal than pyrene or a higher propensity for retrogressive reactions. PHP added to coal/ANT effectively blocked some of the retrogressive reactions of ANT and increased coal conversion from 13% for the binary system to 73% for the ternary system. Substantial hydrogenation of ANT occurred resulting in DHA and THA. PYR was formed from PHP.

The ternary system employing coal/PYR/PHP yielded substantial coal conversion, ~ 83%, which was quite similar to that obtained for coal/PHP of 86%. However, it is difficult to ascertain what occurred with PYR and PHP. An equal weight amount was charged and no net change in their amounts was observed. However, the error in this reaction was much higher than other ternary and binary systems indicating variability in the products produced. The chemistry of the coal/PYR/PHP system was conducive for coal conversion while the coal/PYR system was not. Hence, the presence of PHP increased coal conversion by possibly transferring hydrogen to the system.

The binary reactions of the model reactants with resid resulted in a substantial influence of the different reactants on the resid. Without added reactants, the resid underwent substantial retrogressive reactions causing 20% of the resid to become THF insoluble. The addition of PHP resulted in much more of the resid remaining THF soluble compared to the resid reacted alone. Neither the addition of ANT nor PYR blocked any of the retrogressive reactions; however, the binary system with PYR kept more of the resid THF soluble (~ 86%) than did the ANT at 79%. These binary systems yielded the same amount of THF solubles as did the resid alone. The ranking of the binary resid/model reactant systems was resid/PHP > resid/PYR > resid/ANT.

In the binary system, PHP transferred hydrogen to the resid with 7% PYR being formed. PYR showed no reactivity, but ANT underwent substantial hydrogenation, accepting hydrogen from the resid and forming both DHA and THA. The hydrogenated products showed some variability in the two different reactions, but regardless, even in the reaction with lowest reactivity, more than 13% hydrogenated products were formed.

The ternary systems involving resid had similar resid conversions of 97% for resid/PHP/PYR and 98% for resid/PHP/ANT. Likewise, 97% conversion was obtained with resid and PHP. Hence, regardless of additive the addition of PHP to resid enhanced resid upgrading and helped to inhibit retrogressive reactions. In the resid/ANT/PHP reaction more than 30% of the ANT hydrogenated yielding DHA and THA as products. More than 10% PYR was produced. The resid/PYR/PHP system, however, showed no net change in the quantity of PYR and PHP present.

The quaternary mixtures yielded similar coal conversions as the ternary system although the reaction with ANT did increase somewhat. Substantial hydrogenation of ANT occurred while 30% PYR was produced. ANT only accepted 22% of the hydrogen released thereby leaving substantial hydrogen for uptake by the coal and resid. In the quaternary systems with PYR and PHP, no net change in the weight percents of the reactants was observed; however, a large variability in the quantities was observed.

Summary and Conclusions

The effect of the different added species on the system performance can be evaluated by comparing the degree of upgrading, % TSD, occurring in each system. The highest degree of upgrading occurred in coal systems in which PHP was present. Likewise, the least amount of degrading occurred in those resid systems that contained PHP. For both coal and residuum PYR had a slightly positive effect on the system while ANT had a negative effect.

The hydrogen donor and acceptor ability of both coal and resid has been demonstrated in this study. When no other donor was present, both coal and resid transferred hydrogen to ANT, yielding partially saturated products. Reactions of PHP alone and in combination with hydrogen acceptors clearly showed that a hydrogen acceptor is required in order for PHP to act as a donor. Hydrogen transfer from PHP to aromatics, coal, and resid was obvious because of their respective conversion and the formation of PYR. The relative reactivity of ANT and PYR is of interest. ANT accepted hydrogen readily and quickly from whatever source was available while PYR was nearly unreactive. Hence, those coals and/or resids with reactive structures such as ANT can readily participate in hydrogen transfer reactions while those coal or resid materials that primarily contain nonreactive or stable species like PYR may not involve themselves as readily in hydrogen transfer reactions. Under the conditions employed in this study, hydrogen transfer was observed from the naphthene PHP to an aromatic ANT, to Illinois No. 6 coal and Maya resid.

Acknowledgement

Table 1. Products Produced from Hydrogen Transfer in Reactions of
Anthracene with Perhydropyrene

Weight Ratio of ANT to PHP	Time (min)	Yield, %			%HYD	Hydrogen Efficiency
		DHA	THA	PYR		
0.166	60	13.3	0	0.34	6.7	101
0.51	60	6.9	0	1.2	3.4	38.1
1.0	60	6.4	0	2.8	3.2	31.2
2.1	60	4.3	0	3.0	2.2	44.9
5.0	60	5.7	0	7.0	4.5	104
6.5	60	5.0	1.0	7.7	3.5	83
9.2	60	4.2	0.8	7.8	2.9	111
0.52	90	6.5	0	1.6	3.3	33.6
1.02	90	4.7	0	2.9	2.4	19.4
2.06	90	4.3	0	3.5	2.2	46.0
5.0	90	6.1	2.0	12.8	5.1	72.0
8.0	90	6.0	2.5	13.2	5.5	108
0.51	180	10.4	0	1.9	5.2	41.7
2.08	180	3.7	0	6.3	1.8	21.2
5.26	180	4.1	0	10.1	2.1	34.3
8.52	180	6.9	1.8	16.1	5.3	81.6

Table 2. Coal and Resid Reaction Products from Thermal Coprocessing Reactions

System	Toluene Solubles (%)	THF Solubles (%)	IOM (%)	Conversion (%)	TSD (%)	Liquid to Solid Ratio
Coal/PHP	75.5±2.2	17.5±0.7	7.0±1.5	85.8±3.2	24.0±3.4	3.1
Coal/ANT	50.0±3.1	14.0±1.7	36.0±1.3	13.4±7.3	-9.0±1.1	1.0
Coal/PYR	58.4±1.6	15.2±2.7	26.4±1.1	38.3±3.7	7.6±4.6	1.4
Coal/ANT/PHP	83.8±1.0	8.2±0.9	8.0±0.1	73.0±1.3	26.8±19	5.2
Coal/PYR/PHP	87.7±1.3	7.1±0.7	5.2±0.5	83.4±1.2	29.1±8.7	7.2
Resid/PHP	92.3±0.3	6.2±0	1.5±0.2	97.4±0.5	-47.6±1.9	12.0
Resid/ANT	77.8±1.0	9.4±0.2	12.8±0.8	78.7±1.7	-69.1±2.8	3.5
Resid/PYR	79.5±3.6	12.6±3.2	7.9±0.5	85.5±1.3	-55.4±4.1	4.0
Resid/ANT/PHP	96.1±0.0	3.0±0.0	0.9±0.0	97.6±0.0	-46.5±1.3	24.6
Resid/PYR/PHP	94.8±0.5	4.1±0.3	1.1±0.2	97.1±0.5	-45.1±9.7	18.4
Resid/ANT/PHP/Coal	83.1±1.2	6.9±0.9	10.0±0.4	80.6±0.1	-6.4±6.5	5.0
Resid/PYR/PHP/Coal	85.5±0.8	6.5±0.5	8.0±0.4	83.6±0.9	6.7±18	5.9
Coal	4.0±1.6	31.2±0.7	64.8±2.3	30.4±3.8	4.3±1.7	0.4
Resid	43.8	35.2	21.0	80.5	-61.8±2.4	0.8

ANT = anthracene; PHP = perhydropyrene; PYR = pyrene
Reaction Conditions: 430°C, 60 minutes, N_2 atmosphere

Table 3. Reactive Products from Model Donors and Acceptors in Thermal Coprocessing

System	ANT	DHA	THA	PHP	PYR	Hydrogen Efficiency
Coal/PHP	89.6±0.1	-	-	89.8±2.4	10.2±2.4	
Coal/ANT	-	7.3±0.1	3.1±1	-	-	
Coal/PYR	-	-	-	-	100.0±0	
Coal/ANT/PHP	56.2±1.0	19.2±2.3	24.7±1.4	84.3±0.9	15.7±0.8	49.7
Coal/PYR/PHP	-	-	-	55.4±8.0	44.6±8.0	
Resid/PHP	82.8±4.2	13.4±4.4	3.8±0.2	93.0±1.5	7.0±1.4	60.6
Resid/ANT	-	-	-	-	-	
Resid/PYR	-	-	-	-	100.0±0	
Resid/ANT/PHP	66.4±0.1	18.5±1.1	15.1±1.0	90.2±0.5	9.8±0.6	
Resid/PYR/PHP	-	-	-	47.8±5.3	52.4±5.4	
Resid/ANT/PHP/Coal	64.5±0.4	14.0±0.4	21.5±0.1	69.7±1.5	30.3±1.6	22.0
Resid/PYR/PHP/Coal	-	-	-	52.5±13.3	47.5±13.3	
Coal	-	-	-	-	-	
Resid	-	-	-	-	-	

* -: none present

CATALYTIC EFFECT ON THE GASIFICATION OF A BITUMINOUS ARGONNE
PREMIUM COAL SAMPLE USING WOOD ASH OR TACONITE AS ADDITIVE

R.C. Timpe, R.W. Kulas, and W.B. Hauserman
Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, ND 58202

Keywords: Gasification, Catalysis, Coal

ABSTRACT

Illinois #6 from the Argonne Premium Coal Sample Program was gasified with and
without catalyst added. Catalyst loading effects and the effect of catalysis on
screen fractions were studied using K_2CO_3 as the catalyst. The reactivity
increased significantly with each 2.8 wt% of additional potassium as potassium
carbonate until there was 11.3 wt% potassium. The reactivity increased slightly
with 14 wt% potassium and again slightly with 17 wt% potassium present. The order
of the reaction with respect to carbon approached zero with the higher catalyst
loading. Wood ash with its high potassium (12 wt%) and calcium content (47 wt%)
was shown to be as good a catalyst as the K_2CO_3. Taconite, an iron ore from
northeastern Minnesota, is plentiful, relatively inexpensive, has the required
characteristics for bed material, and may be a potential catalyst. In this test
series, however, it exhibited only slight catalytic effects.

Beulah-Zap lignite from the Argonne Premium Sample Program was gasified with and
without wood ash additive as a basis for comparison with Illinois #6 reactivities.

INTRODUCTION

Catalyzed and uncatalyzed steam gasification of low-rank coals (LRCs) to produce
hydrogen-rich gas streams is a well-known process and is in commercial use today
in this country (Dakota Gasification Plant, Beulah, North Dakota) and abroad. The
successful process produces synthesis gas from which methane is produced to
supplement clean-burning natural gas supplies. Besides augmenting transportable
energy supplies, gasification provides a means of controlling undesirable
emissions from coal utilization processes. Sulfur from the gasified coal is
contained within the plant and is a by-product of the process. Steam gasification
offers a means of utilizing high-sulfur (noncompliance) coals in such a way as to
entrain and remove sulfur gasses before they are released to the atmosphere. As
environmental standards become more rigid regarding sulfur emissions, gasification
as a means of utilizing higher sulfur content coals may become more attractive.

Low-rank coals make good gasification feedstock due to inherent catalysts in the
form of salts of alkali and alkaline earth elements and due to their reactive
organic functionalities. These components give LRCs first order carbon
reactivities of > 2 hr^{-1} at 750°C (1). Raw low-rank coals have consistently been
shown to have higher reactivities in the gasification process than bituminous
coals. Gasification of bituminous coals could become feasible if the reactivity
of those coals with their greater carbon content/lb could be increased. Catalysis
brought about by alkali and alkaline earth additives has been shown to increase
the reactivities of these coals (2,3). Cost and availability of catalytic
materials is a major concern when catalysis is required. As a result, reactivity,
and supplies of inexpensive potential additives needed to increase that
reactivity, becomes a primary consideration in selecting gasification feedstock.
Several plentiful, naturally occurring materials (minerals) are available,
including nahcolite, trona, halite, limestone, dolostone, potash, saltpeter, and

sunflower seed hulls; most of which have been investigated as catalysts (4,5). The first three mentioned minerals are rich in sodium, the next two are rich in calcium, and the last three are rich in potassium, all of which are known to be good catalysts for the coal gasification reaction. Potassium and sodium have proven to be the best catalysts of this group. The advantage of using sodium is that its mineral deposits are much more common than potassium mineral deposits, making the former less expensive. The major disadvantage of sodium is the agglomeration of particles and the ash fouling that it causes. Although it is more expensive, potassium appears to cause less operational problems. Therefore, if a source can be found that is less expensive than sources now available, and if recycling of the potassium can be made possible, potassium will become the best choice of catalyst from the alkali-alkaline earth materials mentioned above. Wood ash which typically has a high potassium content may be such a catalyst.

Transition metals have also been shown to catalyze the coal gasification reaction. Taconite, a metal ore from Minnesota, is plentiful, inexpensive, and rich in iron, making it a candidate for a gasification additive.

This paper reports the results of a bench-scale study of steam-char rate enhancement conferred to Illinois #6 from the Argonne Premium Coal Sample Program by the presence of potassium carbonate (K_2CO_3), wood ash, or taconite. An Argonne sample of Beulah-Zap lignite was gasified and reported on for comparison.

EXPERIMENTAL

The coals tested were Illinois #6 (Herrin seam) and Beulah-Zap (Beulah-Zap seam) from the Argonne Premium Coal Sample Program. They were received in 10-gram lots in sealed vials and were used directly from the vials without further preparation, other than catalyst addition. Unused sample was stored under inert gas in sealed 20-mL scintillation vials. Proximate and ash analysis are shown in Table 1.

Ten weight percent dry catalyst was admixed with each coal to be tested. Dispersal of the catalyst was accomplished by shaking the coal-additive mixture vigorously in closed vials for ca. ten minutes. The catalysts were prepared by combustion in air. Hardwood (cottonwood and aspen) ash was prepared in a small batch. The cottonwood/aspen ash was the remnants of a domestic fireplace fire. The plywood ash was provided by Northwood Panelboard Co, Solway, Minnesota.

Approximately 40 milligrams of coal or coal/catalyst material is loaded onto the pan of the DuPont 951 thermogravimetric analysis microbalance module. The quartz tube enclosing the pan and serving as the reaction chamber is secured by a knurled nut to the balance housing. The reaction chamber is purged with an ambient pressure argon flow at ca. 160 cm^3/min. The sample is heated at ~100°C/min to the target temperature at which point the $H_2O_{(g)}$ flow is introduced through the side arm of the quartz tube, and argon flow is reduced to ca. 60 cm^3/min. The reaction was carried out at 700°, 750°, and 800°C. Total gas effluent can be collected in a gas bag for analysis by GC. Weight, time, and temperature are stored by the DuPont 1090 data station for later data reduction.

RESULTS AND DISCUSSION

Illinois #6 and Beulah-Zap lignite from the Argonne Premium Coal Sample Program were gasified with and without catalyst added. As shown in Table 2, the uncatalyzed bituminous coal char had typical low reactivities with steam in the 700°-800°C temperature range when compared with those of low-rank coal. The uncatalyzed Beulah-Zap reactivities at each of the three temperatures were 40-50 times greater than those of the Illinois #6. However, in the presence of only 1-2 wt% added potassium, the difference was reduced to < ten times and with 5 wt% added potassium, .< 2 times.

Catalyst loading effects and the effect of catalysis on screen fractions of Illinois #6 were studied using K_2CO_3 as the model catalyst. The reactivity increased significantly with each 2.8 wt% of additional potassium as potassium carbonate, until there was 11.3 wt% potassium as shown in Figure 1. As potassium concentrations were increased to 14 wt% and 17 wt%, the reactivity increased only slightly. As the catalyst loading was increased, the dependence on carbon concentration decreased. The order of the reaction with respect to carbon approached zero with the higher catalyst loading, as shown in Figure 2.

Illinois #6 was sieved to get size fractions for reactivity testing. The fractions collected were +60 mesh (>0.250 mm), -60x100 mesh (0.250>p>0.149 mm), -100x140 mesh (0.149>p>0.105 mm), -140x200 mesh (0.105>p>0.074 mm), and -200x325 mesh (0.074>p>0.044 mm). Figure 3 shows the reactivity as a function of those sieve fractions.

Hardwood ash with its high potassium (12 wt%) and calcium content (47 wt%) was shown to have promise as a catalyst. Increased reactivity brought about by dry wood ash was slightly less than that of an equivalent amount of K_2CO_3, but the application of dried aqueous extract of the ash containing 39 wt% potassium did provide an equivalent increase in reactivity. Taconite, an iron ore from northeastern Minnesota, is plentiful, relatively inexpensive, and has the required characteristics for a bed material, and may be a catalyst for the coal char-steam reaction. In this test series, however, it exhibited only slight catalytic effects.

Illinois #6 agglomerated when heated to the gasification temperatures. However, addition of K_2CO_3 to the coal resulted in no observable agglomeration. A similar effect was noted on addition of the hardwood ash as a reaction catalyst, whereas addition of the ash from a plywood plant did not prevent agglomeration. Table 3 shows the elemental analyses of the ash from the coal with 10 wt% additive. The softening and collapsing of pores during agglomeration and subsequent decrease in surface area is at least partially responsible for the low reactivity of the coal. The addition of potassium carbonate and the hardwood ash resulted in decreased agglomeration as well as an increase in reactivity, whereas the ash from the plywood facility had little effect on either.

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TABLE 1

PROXIMATE AND ASH ANALYSES OF ILLINOIS #6 BITUMINOUS AND
BEULAH-ZAP LIGNITE FROM THE ARGONNE PREMIUM COAL SAMPLE PROGRAM

Sample	Illinois #6 Raw (TGA)		Beulah-Zap Raw (TGA)	
	AR	MF	AR	MF
Moisture, wt%	9.41	--	32.66	--
Volatiles, wt%	34.75	38.36	30.19	44.83
Fixed C, wt%	41.08	45.35	30.67	45.54
Ash, wt%	14.76	16.29	6.49	9.64

XRF Analysis of Coal Ash

Element	Ill. #6		Beulah-Zap	
	% of Ash	% of Coal	% of Ash	% of Ash
Silicon	20.43	3.33	8.88	0.86
Aluminum	9.68	1.58	5.35	0.52
Iron	12.59	2.05	5.88	0.57
Titanium	0.60	0.10	0.42	0.04
Phosphorous	0.09	0.01	0.31	0.03
Calcium	5.64	0.92	16.72	1.63
Magnesium	0.72	0.12	6.27	0.61
Sodium	0.00	0.00	4.01	0.39
Potassium	2.41	0.39	0.33	0.03
Sulfur	2.72	0.44	6.37	0.62

TABLE 2

REACTIVITIES OF UNCATALYZED AND CATALYZED COAL CHAR WITH STEAM*

Catalyst	Illinois #6						Beulah-Zap	
	None	K_2CO_3	A[1]	B[2]	C[3]	Tac.	None	A[1]
				k, hr^{-1}				
Temp, °C								
700	0.06	--	--	--	--	--	2.30	3.64
750	0.15	4.36	--	--	3.01	0.41	7.76	8.67
800	0.33	--	0.35	0.54	--	--	14.61	10.41
E_a, kcal/mol	5.57						38.53	

* Assumed 1st order with respect to carbon.
[1] A Provided by Northwood Panelboard Co.
[2] B Residue from combustion of cottonwood/aspen.
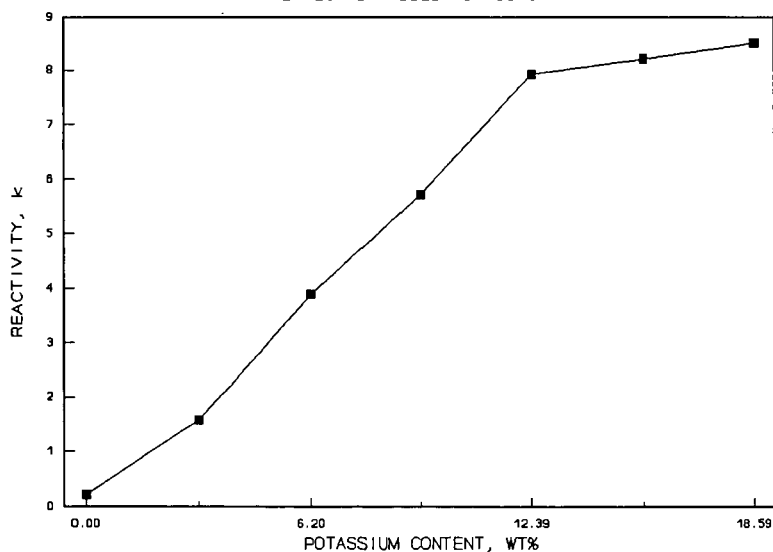[3] C Aqueous extract of hardwood ash.

TABLE 3

XRF ANALYSES OF ASH FROM COAL +10WT% CATALYST, wt%

XRFA Results	Ill. #6	B-Zap	w/Ill. #6 Ash B	w/Ill. #6 Ash A	w/B-Zap Ash A
Silicon	3.33	0.86	4.49	5.04	2.58
Aluminum	1.58	0.52	1.95	1.97	1.77
Iron	2.05	0.57	2.26	2.22	2.27
Titanium	0.10	0.04	0.14	0.12	0.11
Phosphorous	0.01	0.03	0.07	0.06	0.02
Calcium	0.92	1.63	3.88	3.39	1.26
Magnesium	0.12	0.61	0.59	0.46	0.16
Sodium	0.00	0.39	0.12	0.07	0.01
Potassium	0.39	0.03	1.12	1.07	0.50
Sulfur	0.44	0.62	0.63	0.57	0.50
Total %	8.94	5.30	15.26	14.97	9.18

Figure 1. Effect of K_2CO_3 catalyst loading on Illinois #6 char-steam reactivity at 750°C.

ILLINOIS #6 CHAR-STEAM REACTION AT 750C

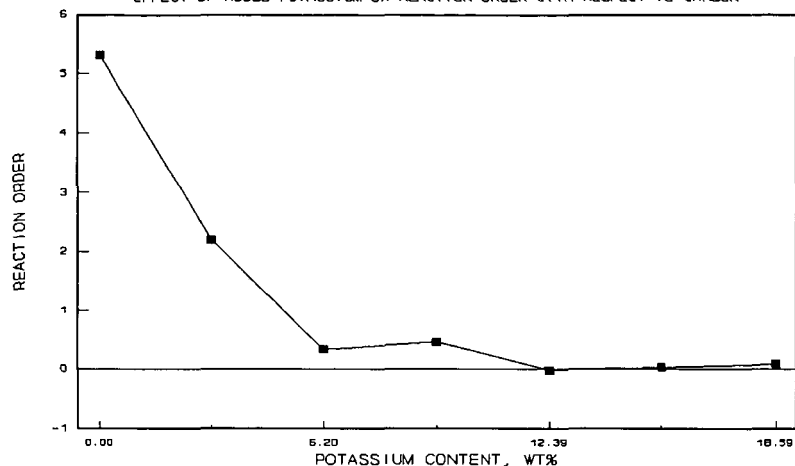EFFECT OF ADDED POTASSIUM ON REACTION ORDER WITH RESPECT TO CARBON

Figure 2.   Effect of potassium loading on order of Illinois #6 char-steam reaction with respect to carbon.

EFFECT OF PARTICLE SIZE ON GASIFICATION OF ILLINOIS #6

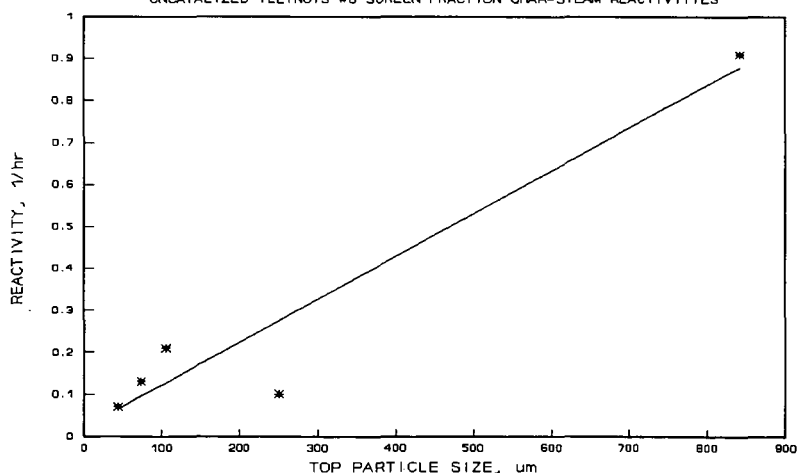UNCATALYZED ILLINOIS #6 SCREEN FRACTION CHAR-STEAM REACTIVITIES

Figure 3.   Effect of exclusion of particle size on Illinois #6 char-steam reactivity.

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